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THE SPECIFIC HEAT OF SOLUTIONS WHICH ARE NOT ELECTROLYTES.

By William Francis Magie.

1. The specific heat of solutions has already been made the subject of extended researches. In one of these, by Schüller,[1] it was found that with mixtures of chloroform, benzene and bisulphide of carbon the heat capacity was equal to the sum of the heat capacities of the two liquids mixed. In the case of alcohol mixed with these liquids or with water no such simple relation held, but the observed heat capacity was higher than that given by this rule. As a part of his famous thermochemical investigations, Thomsen[2] studied the specific heats of about thirty aqueous solutions of acids and salts. Besides giving the observed specific heat, Thomsen calculated the apparent molecular heat of the dissolved substance or solute by subtracting the heat capacity of the water in the solution from the total heat capacity and determining from this difference the apparent heat capacity of a mass of the solute which was equal to its molecular weight. This apparent molecular heat diminished as the dilution was increased, even in many cases becoming negative. This result was confirmed by Marignac,[3] who found besides that with aqueous solutions of sugar and with solutions of sulphur, phosphorus and iodine in bisulphide of carbon, the molecular heats were constants

[1] Pogg. Ann. Ergänzungsband, V., p. 116, 1871.
[2] Pogg. Ann., 142, p. 337, 1871.
[3] Ann. de Chem. et de Phys., 4 Ser., XXII., p. 385, 1871.

for every concentration. As will be seen from the following discussion, the reason for the differences observed in these solutions lies in their different behavior with respect to osmotic pressure.

2. In this discussion we shall use the method applied by van't Hoff to the study of the molecular depression of the freezing point. The solution considered is supposed to be made up by dissolving n gram-molecules of the solute in N gram-molecules of the solvent (a gram-molecule is a weight of the substance in grams equal to its molecular weight). Let the solution, the mass of which is W, be enclosed in a vessel furnished with a semipermeable wall, and so arranged that pressure may be exerted upon it by means of a piston. By the aid of this vessel and the proper accessory reservoirs of heat the following reversible operations may be performed.

By exerting the pressure p_0 upon the solution we may force out some of the pure solvent through the semipermeable membrane. The diminution in volume of the solute will entail a development of heat, and, to keep the temperature constant at the original temperature t_0, this heat must be abstracted. Let us designate by $\mu_0 dv$ the heat which must be abstracted to keep the temperature constant, while the volume is diminished by dv. Then μ_0 may be called the latent heat of expansion. The compression is continued until a mass w of the solvent is removed from the solution. The work done by the external pressure is $\int_{v'}^{v''} p_0 dv$ and the heat abstracted is $\int_{v'}^{v''} \mu_0 dv$, when v' and v'' are the volumes of the original solution and of the more concentrated solution after the mass w of the solvent is removed.

We then cool the solution and that portion of the solvent which is outside the vessel to the slightly lower temperature t. To do this we remove the quantities of heat $s''(W - w)(t_0 - t)$ and $sw(t_0 - t)$ from the solution and the solvent respectively. The symbols s'' and s represent the specific heats of the solution and the solvent respectively.

We then allow the solvent to enter the vessel again through the membrane. By this operation work is done against the external pressure p, which may be different from p_0 because of the difference

of temperature, and heat is consumed, which must be supplied from without to keep the temperature constant. Using similar symbols to those already introduced, we shall represent the work done by $\int_{v''}^{v'} p dv$, and the heat supplied by $\int_{v''}^{v'} \mu dv$. In this statement we ignore the slight change of volume of the liquids due to the difference of temperature.

We then raise the temperature of the solution, which now contains all the solvent, to the original value t_0. To do this we introduce the quantity of heat $s' W(t_0 - t)$ where s' is the specific heat of the original solution.

By these operations, which are all reversible with respect to the liquids serving as the working substance, we have brought the system back to its original state. We may, therefore, write the equations of energy and entropy for this cycle. To form the first of these we set the heat removed from the system equal to the work done upon it, and have, on rearranging the terms,

$$(a) \quad \int_{v''}^{v'} (\mu_0 - \mu) dv + \{s''(W - w) + sw - s' W\}(t_0 - t) = \int_{v''}^{v'} (p_0 - p) dv.$$

The second equation is formed by substituting in the equation $\int \frac{dQ}{T} = 0$ the appropriate values of dQ and of T for each of the four operations. If the temperatures t_0 and t are taken on the absolute scale, this equation becomes

$$(b) \quad \int_{v''}^{v'} \left(\frac{\mu_0}{t_0} - \frac{\mu}{t} \right) dv + \{s''(W - w) + sw - s' W\} \int_{t}^{t_0} \frac{dt}{t} = 0.$$

Now $\int_{t}^{t_0} \frac{dt}{t} = \log \frac{t_0}{t} = \frac{t_0 - t}{t}$, if the difference of temperature is so small that we may neglect all terms in the expansion beyond the first. Hence (b) becomes

$$(c) \quad \int_{v''}^{v'} \left(\frac{\mu_0}{t_0} - \frac{\mu}{t} \right) dv + \{s''(W - w) + sw - s' W\} \frac{t_0 - t}{t} = 0.$$

Now v and t are independent, so that we may introduce t as a factor in the integral with respect to v, and hence from (a) and (c) we get

$$(d) \qquad \int_{v''}^{v'} \mu_0 \left(\frac{1}{t} - \frac{1}{t_0}\right) dv = \int_{v''}^{v'} \left(\frac{p_0 - p}{t}\right) dv.$$

It was shown by van't Hoff, and his conclusion has been repeatedly confirmed, that the osmotic pressure in many solutions is proportional to the absolute temperature. If the pressure exerted in the operations described is the osmotic pressure and if it obeys this law we may set in (d) $\frac{p}{t} = \frac{p_0}{t_0}$, or $\frac{p_0 - p}{t} = p_0 \left(\frac{1}{t} - \frac{1}{t_0}\right)$, and obtain (e) $\mu_0 = p_0$; or, the osmotic pressure equals the latent heat of expansion. This relation is well known and has been frequently assumed as the basis of a demonstration that the osmotic pressure is proportional to the absolute temperature.

Using this in (a) or (b) we obtain

$$(f) \qquad s''(W - w) + sw = s'W,$$

a relation which shows that the heat removed in the second operation is equal to that introduced in the fourth.

3. The relation here found is equivalent to the law that the specific heats of the solvent and of the solute are constant at all concentrations. For, let us call the masses of the solvent and of the solute in the original solution M and m respectively, and let us use σ to designate the specific heat of the solute in the solution. Then by the law just stated we may write for the heat capacity of the solution before and after the mass w of the solvent has been removed

$$(g) \qquad \begin{cases} s'(M + m) = sM + \sigma m \\ s''(M - w + m) = s(M - w) + \sigma m \end{cases}$$

from which we get (f), since $W = M + m$.

4. This law has been deduced from the assumption that the solute exerts a pressure under the following limitations:

1. The pressure exerted by the solute must be proportional to the absolute temperature.

2. The work done against any external pressure, say that of its own vapor, in forcing out the solvent, is neglected.

3. The specific heats are supposed to be independent of the temperature.

4. The change of volume consequent upon change of temperature is neglected.

Of these the first is the only one that has been formally introduced into the equations. According to the investigation of Schiller [1] the second introduces a term which is of the second order of small quantities and is assumed by him to be negligible. There are no data at hand by which we can examine this matter fully, but I hope to be able to consider it at some future time. It may be that this term is involved in the explanation of the behavior of such solutions as those of alcohol in water, in which solution is attended with a considerable change of temperature and diminution of volume. In these cases, however, it seems that the pressure which must be exerted to force out the solvent will not be that merely which is required to compress the solute as a gas, but different from that, in consequence of the molecular interactions between the solute and the solvent, and that this pressure may be a function of the temperature which does not conform to the first condition.

It is one of the fundamental propositions of the modern theory of solutions that non-electrolytes in solution exert an osmotic pressure which is proportional to the absolute temperature, and if these substances do not develop or absorb heat on going into solution it seems probable that the pressure needed to force out the solvent is equal to the osmotic pressure; so that such solutions should exhibit specific heats that conform to the simple law stated above. Electrolytes should also conform to the law when the dissociation is complete. But before dissociation is complete, it would seem that the osmotic pressure of electrolytes should not be exactly proportional to the absolute temperature. Certainly the dissociation of a gas is a function of temperature as well as of volume, and there does not seem to be any essential distinction between the dissociation of a gas and that of an electrolyte in solution. Furthermore, the change of electrical conductivity with temperature is such as to indicate a connection between the dissociation and the temperature.

It is true that the founders of the theory of solutions considered Gay-Lussac's law applicable to electrolytes as well as to non-electrolytes, and cited the measurements of Pfeffer and others in sup-

[1] Wied. Ann., Vol. 67, p. 299, 1899.

port of this view. All that can be said at present in this connection is that the evidence for this view is incomplete. In comparisons of isotonic solutions with each other it may have happened that the change of dissociation was nearly the same in both solutions, so that they remained isotonic without conforming precisely to Gay-Lussac's law. Most of the direct measurements show a departure from Gay-Lussac's law, which is slight, to be sure, but still perhaps sufficient to account for the variability of the specific heats of electrolytic substances. Moreover, the experiments on osmotic pressure were carried out with solutions which were more dilute, as a rule, than those used in the determinations of specific heats, and the more dilute solutions should conform more closely to Gay-Lussac's law.

5. In case the pressure is not proportional to the absolute temperature, we may return to equation (a), which holds in any case. If we divide by $t_0 - t$, and remember that $t_0 - t$ may be as small as we please, we have in the limit,

$$\lim. \frac{\mu_0 - \mu}{t_0 - t} = \frac{d\mu}{dt} \lim.; \quad \frac{p_0 - p}{t_0 - t} = \frac{dp}{dt}.$$

We may then write (a) in the form

$$(h) \qquad s''(W - w) + sw - s'W = \int_{v''}^{v'} \left\{ \frac{dp}{dt} - \frac{d\mu}{dt} \right\} dv.$$

But from the known thermodynamic relation $\frac{\partial Q}{\partial v_t} = t \frac{\partial p}{\partial t_v}$, in which $\frac{\partial Q}{\partial v_t} = \mu$, we may deduce $\frac{d\mu}{dt} = \frac{dp}{dt} + t \frac{d^2p}{dt^2}$, and substituting in ($h$) we have

$$(j) \qquad s''(W - w) + sw - s'W = - \int_{v''}^{v'} t \frac{d^2p}{dt^2} dv.$$

Now if we know the specific heats at different concentrations we may calculate from our observations

$$(k) \qquad \begin{cases} \zeta' = s'(M + m) - sM \\ \zeta'' = s''(M - w + m) - s(M - w), \end{cases}$$

following the analogy of (g), except that ζ' will not be equal to ζ''. In these equations ζ' and ζ'' are the *apparent* heat capacities of the

solute, on the hypothesis that the specific heat of the solvent remains constant. They become the apparent molecular heats when m is the mass of one gram-molecule of the solute. From them we get

$$\zeta'' - \zeta' = s''(W - zv) + szv - s'W$$

and hence

$$(l) \qquad \zeta' - \zeta'' = \int_{v''}^{v'} t \frac{d^2p}{dt^2}\, dv.$$

6. Now, as may easily be shown, $\zeta' - \zeta''$ is the difference between the heat capacities of the system in its two states. Since it is a function of the volume of the solution, we may write

$$\zeta' - \zeta'' = \int_{v''}^{v'} \frac{dc}{dv}\, dv$$

where c is the heat capacity, and hence, dropping the integral signs,

$$(m) \qquad \frac{dc}{dv} = t \frac{d^2p}{dt^2}.$$

From this it follows, when $p = t \cdot \text{cons.}$, since then $\frac{d^2p}{dt^2} = 0$, that $\frac{dc}{dv} = 0$, which expresses the result in the special case of non-electrolytes.

In this form the results given in the preceding sections were recently published by N. Schiller.[1] They were presented by me to the Princeton Science Club on May 12, 1898, and were published in abstract in the *Princeton University Bulletin* for January, 1899. The delay in publication was due to my desire to confirm the conclusions of theory by experiment. The observations recorded in this paper were begun in November, 1898.

7. I have not been able as yet to do more than examine certain non-electrolytic solutions. In general the results obtained with these confirm the law expressed in equations (g) or (f), § 4. Where they do not do so, as in the case of solutions of which alcohol is a constituent, further study of the properties of the solutions will be needed before the theory, in the form given in equation (l), can be tested. For electrolytic solutions the investigations of

[1] Wied. Ann., Vol. 67, p. 259, 1899.

Thomsen and Marignac furnish a wealth of material. In these cases also the properties of these solutions must be studied further before the theory can be tested as it applies to them.

8. The method used in the determination of the specific heat was a modification of Pfaundler's method.[1] This method consists essentially in the communication of equal quantities of heat to two similar calorimeter vessels, one containing the standard liquid and the other, the liquid to be observed. The communication of equal

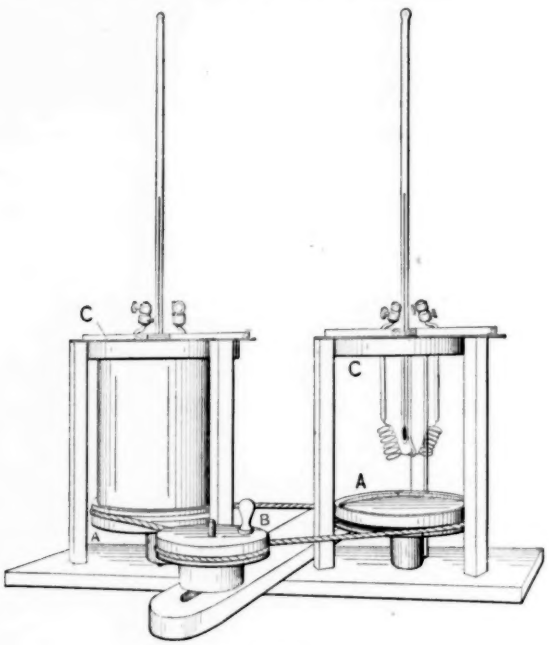

Fig. 1.

quantities of heat is accomplished by passing an electrical current through two coils of equal resistance, one of which is immersed in each liquid. In the experiments to be described this method is especially convenient, for, since the quantity ultimately desired is the molecular heat of the solute, the solvent can be used as the standard, and a suitable adjustment of the weights of the standard and of the solution under examination brings about a nearly equal rise of temperature in both calorimeters. In this case, since the

[1] Wien. Acad. Bericht., Vol. LIX., 1869.

calorimeters are similar, the corrections for the calorimeter constants and for radiation become negligible.

The calorimeters (Fig. 1) were cylindrical cups of thin brass, four inches in diameter and six inches high, weighing with the stirrers hereafter to be described, 176 grams each. They were set upon a network of fine cord within larger brass vessels, six inches in diameter and eight inches high, and were centered by three wooden pins projecting from rings that fitted within the exterior vessels. Only one of these vessels is shown in the figure. These exterior vessels, or shields, were set on horizontal wooden disks, *A*, mounted on spindles ast urn-tables and arranged so as to be rotated in the same sense and at the same rate by a cord passing around their circumferences and over a wheel *B*, fixed to an offset from the base. At the bottom of each of the calorimeters was placed a stirrer, Fig. 2, *A*. This consisted of a brass fan or screw made up of four blades radiating from the center and set at an angle of about 60° from the vertical. A part of the lower portion of each blade was cut away so as to prevent the accumulation of liquid between it and the bottom of the vessel. This stirrer was made to fit tight in the calorimeter vessel and was held in position by friction. It was found that when the calorimeters were rotated, the interference of the resistance coils and thermometers with the free motion of the liquids combined with the effect of the stirrers to produce a turbulent motion sufficient to keep the liquids thoroughly mixed. The stirring could be promoted by occasionally changing the sense of the rotation. This method of stirring proved itself highly satisfactory. No errors in the results could be traced to insufficient mixing of the different parts of the liquid.

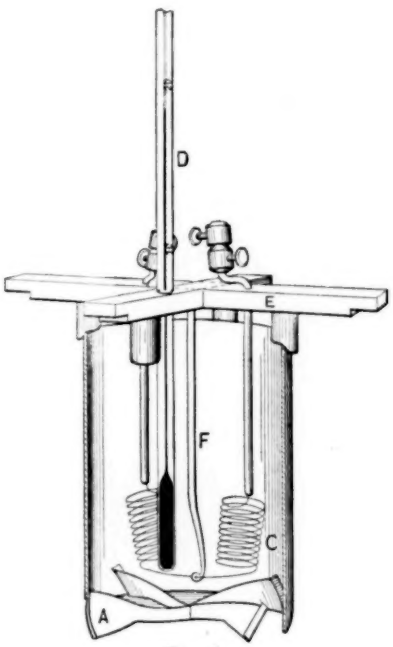

Fig. 2.

The resistance coil, Fig. 2, *C*, and thermometer, *D*, for each calorimeter were carried by a light cross of wood, *E*, the ends of which rested on a ring of tin, Fig. 1, *C*, supported above the vessels by wooden pillars. The coil and thermometer were therefore held fixed, while the calorimeter vessel rotated about them. On the arms of the cross, in suitable positions, were fastened blocks of cork, which cleared the upper edge of the vessel by perhaps an eighth of an inch when it was in position, and which served to support the coils, etc., when the calorimeter was removed from its place for weighing or cooling. It is in this latter condition that the calorimeter is represented in Figure 2. The coil was a spiral of special German silver wire No. 24 B. & S. with a resistance of about 4 ohms and with an exceedingly small temperature coefficient. This wire was very obligingly furnished me by Mr. Edward Weston of the Weston Electrical Instrument Company of Newark, N. J. The ends of the spiral were attached to heavy copper wires, and the middle of the spiral was held down nearly to the bottom of the vessel by a hook made in the end of a glass tube F, drawn out into a thin stem and fixed to the cross. The two parts into which the spiral was thus divided were each of them rigid enough to hold their positions without any appreciable yielding. The copper rods supporting the spiral were fixed near the two extremities of the arm of the cross, and their upper ends were bent in so as to fit into the mercury cups of a Carey Foster Bridge. By means of this bridge the resistances of the two coils could be compared and adjusted whenever required.

The thermometer was borne by the other arm of the cross and was placed about half way between the vessel and its walls. The upper end of its bulb was generally immersed about an inch below the surface of the liquid.

9. The thermometers were made by Green and were carefully compared with a standard whose corrections were furnished by the Reichsanstalt. Their curves of correction showed similar variations in all parts of the scale used, indicating the care with which the tubes were calibrated. The thermometers were graduated on the stem; that used in calorimeter A being divided into tenths, that used in calorimeter B to twentieths of a degree. They were read by means of lenses carried in adjustable clamps, and care was taken

to avoid parallax by bringing the reflection of the mark nearest the end of the mercury column behind the mark itself. They were tapped, before a reading was taken, with a light cork hammer, some trials which were made on a falling column indicating that this was an important precaution. The readings were made by estimation to hundredths of a degree. The coarseness of the marks on the stem rendered this estimation difficult in certain positions of the mercury column, and I do not dare to say that the observations are exact to the hundredths of a degree.

10. In repeating an observation with the same liquids it is necessary to cool the calorimeters to a common initial temperature. To accomplish this most easily and quickly of two rotating turntables were constructed, similar to those already described, but of larger diameter, and furnished with similar rings to support the crosses with their coils and thermometers. On each of these tables was placed a cylindrical copper vessel eight and one-half inches in diameter and six inches high. Within this vessel stood a cylinder of coarse wire netting centered by three projecting arms. Its diameter was such that it easily received the calorimeter vessel. The space between the wire cage and the external walls was packed with snow or broken ice, and it was found advantageous to fill the vessel about one-third full with water. The calorimeters placed in the wire cylinders were quickly cooled to the desired temperature and a little experience made it easy to remove them at such times that their final temperatures did not differ by more than one or two tenths of a degree.

11. The current for the coils was furnished by a dynamo-machine. A contact maker, a Weston ammeter and a variable resistance of coarse German silver wire, with a sliding contact, were included in the circuit. The current remained fairly constant during a set of observations. In different cases it varied from 4.2 to 5.2 ampères.

12. The weighings were performed on a large balance, which was sensitive to 5 mg. with a load of 1 kilogram.

13. The course of a set of observations was as follows :

After it had been determined what was the proper amount of solution to be used to give approximately equal temperature changes in the two calorimeters, the calorimeters, with their coils and ther-

mometers, were placed in turn on the balance and were filled with the solution and the solvent respectively, care being taken that enough liquid was used to well cover the coils and the bulbs of the thermometers. The calorimeters were then placed in the coolers and withdrawn when the desired temperature was reached. If possible this temperature was so determined that the rise to the room temperature was equal to that allowed beyond the room temperature in the observation. This was not always convenient, and in view of the similarity of the two calorimeters and the consequent equality of their radiation coefficients, no great stress was laid on attaining this condition. The calorimeters were wiped dry and placed in their respective positions. If after a few rotations of the turntables it was found that their temperatures differed by more than two-tenths of a degree, this difference was adjusted by warming the cooler one in the hands. The connections with the coils were then made and the vessel rotated for thirty seconds, after which the thermometers were tapped and read as quickly as possible. The rotation was then resumed and after the lapse of one minute from the stoppage of the first rotation, the thermometers were read again. If any irregularity in the rise of the thermometers was observed this process was repeated, but ordinarily these two readings sufficed to fix the initial temperature. The current was then thrown in, and the calorimeters rotated, care being taken to change the sense of rotation every now and then. When the desired elevation of temperature was nearly reached, the current was cut off and the rotation continued for thirty seconds. To render the conditions in this part of the observation as nearly the same as possible for all the observations, the rotation was carried out for ten seconds in one sense, then reversed for ten seconds, then carried out for five seconds in the first sense, and again reversed for five seconds. The thermometers were then tapped and read. After the lapse of one minute, during most of which the rotation was continued, a second reading was made, and a third after the lapse of another minute. These readings were made to test the loss of heat by radiation and evaporation, and to furnish the basis for an estimate of the true final temperature.

The calorimeters were then, if the solvent was, like water, suffi-

ciently volatile to lose weight appreciably during this series of operations, replaced on the balance, and enough of the solvent added to restore the original weights; after which they were cooled, and the observations repeated. In most cases four observations were made with one solution.

14. It was found that water acted upon the brass vessels and the German silver coils sufficiently to conduct as an electrolyte and so to change the resistance of the coils. To avoid this the coils were dipped in melted paraffine, which sheathed them with an insulating coating. No delay in assuming the proper final temperature could be detected on the part of the liquid due to the low heat conductivity of this paraffine coating, and it served its purpose well in preventing changes of resistance in the coils. This precaution was also needed with alcohol, but was unnecessary with aniline. If the resistances of the coils differed by more than a certain amount a correction to the result became necessary. This difference was, however, outside the limits within which the resistances could easily be adjusted, and was rarely, if ever, allowed.

15. The ratio of the specific heats of the liquids in the two calorimeters could be calculated immediately from the formula $\frac{m_2 t_2}{m_1 t_1}$, where m_1 and m_2 represent the masses of the solution and the solvent as standard, t_1 and t_2 the changes of temperature in these masses respectively. The corrections due to the calorimeter constants, to radiation and to the resistances of the coils are all differences of quantities nearly equal for the two similar calorimeters, and may be neglected. The specific heat of the solution was then found by multiplying this ratio by the specific heat of the solvent. From this the specific and the molecular heat of the solute were obtained, by assuming that the specific heat of the solvent in the solution remains unchanged. Since the ratios of the specific heats thus obtained are always very nearly equal to unity, the calculated molecular heats of the solute are not seriously affected by any small error in the assumed specific heat of the solvent. This may, therefore be taken from published tables or results, without requiring a special investigation.

16. The results obtained for the specific heats of the solutions

examined are given in the following tables. The apparent molecular heats of the solutes, given under the symbol ζ, were calculated by assuming that the specific heat of the solvent is unchanged in the solution. The column headed by N gives the number of gram-molecules of the solvent containing one gram-molecule of the solute. The calculated specific heats are those determined from equation (g) by using for σ, the specific heat of the solute, the mean specific heat found from the mean value of ζ.

17. *Cane Sugar in Water.*—The sugar employed was prepared by recrystallization of rock candy. The best crystals were selected, powdered, and carefully dried in a steam bath. The water, as in all cases in which water was used, was distilled in a block tin tube on the plan introduced by Hulett,[1] and was shown, by observations of its electrical conductivity, to be of a high degree of purity. Its molecular weight was taken to be 18.

Cane Sugar ($C_{12}H_{22}O_{11}$) *in Water. Molecular Weight* 342.

N	s' Observed.	s' Calculated.	ζ
50	0.8479	0.8475	153.1
100	0.9115	0.9116	152.5
150	0.9375	0.9377	150.
250	0.9609	0.9609	152.7
Mean molecular heat,			152.6

The mean molecular heat obtained by Marignac for cane sugar was 147.

18. *Dextrose in Water.*—The dextrose was obtained from Kahlbaum. The very slight trace of water which it contained was removed by long drying in a steam bath.

Dextrose ($C_6H_{12}O_6$) *in Water. Molecular Weight*, 180.

N	s' Observed.	s' Calculated.	ζ
100	0.9490	0.9489	79.
200	0.9731	0.9732	78.4
300	0.9819	0.9819	79.
Mean molecular heat,			78.8

[1] Journal of Chem. Physics, September, 1896.

19. *Glycerine in Water.*—The glycerine was c. p. glycerine obtained from Merck. About equal volumes of this glycerine and of water were mixed and the specific gravity determined by a standardized Mohr's balance. From this the percentage composition of the solution was found by the use of Gerlach's table (Landolt and Börnstein, p. 230), and the solutions used were made up from this stock solution. By a comparison of the weight of water added with that indicated by the specific gravity, the amount of water in 100 grams of the glycerine was determined to be 1.94 grams.

Glycerine ($C_3H_8O_3$) *in Water. Molecular Weight* 92.

N	s' Observed.	s' Calculated.	ζ
40.40	0.9556	0.9537	55.6
50.275	0.9621	0.9620	54.2
88.49	0.9771	0.9775	53.4
100.	0.9803	0.9800	54.7
132.96	0.9841	0.9847	52.3
150.	0.9867	0.9864	55.0
250.	0.9917	0.9918	53.9
400.	0.9948	0.9948	54.0
500.	0.9954	0.9958	50.0
Mean molecular heat,			54.1

In taking this mean the result for $N = 500$ was omitted.

20. *Mannite in Water.*—The mannite was obtained from Merck. No pains were taken to dry it or to test its purity.

Mannite ($C_6H_{14}O_6$) *in Water. Molecular Weight* 182.

N	s' Observed.	s' Calculated.	ζ
100	0.9662	0.9647	115
200	0.9812	0.9815	113
300	0.9873	0.9875	111
400	0.9900	0.9905	108
Mean molecular heat,			112

These molecular heats show a regular decrease with increasing dilution. I believe that this change is only apparent and not real. In the first place the results for $N = 100$, 200, 300 involve a correction, determined after the last result was obtained, that was as-

sumed to be constant, but may very well have had an increasing value; and in the second place, if the mannite were not perfectly dry, the effect of the water contained in it would be least felt in the more dilute solutions. In my opinion the most probable value for the molecular heat of mannite in water is 108.

21. *Urea in Water.*—The urea was obtained from Merck, in the form of clean, sharp-edged, separate crystals. A similar specimen to that used was dried in a steam bath and showed only an almost inappreciable amount of water present.

Urea (CON_2H_4) *in Water. Molecular Weight* 60.

N	s' Observed.	s' Calculated.	ζ
100	0.9796	0.9790	22
200	0.9896	0.9893	22
300	0.9927	0.9929	20
400	0.9945	0.9946	20
Mean molecular heat,			21

22. *Acetamide in Water.*—The acetamide was obtained from Merck. It was found to be dry. When dissolved it cooled the water slightly.

Acetamide $C_2H_3O(NH_2)$ *in Water. Molecular Weight* 59.

N	s' Observed.	s' Calculated.	ζ
100	0.9870	0.9868	34.9
200	0.9931	0.9933	34.
Mean molecular heat,			34.5

23. *Ethyl Alcohol in Water.*—The alcohol was Squibb's c. p. alcohol, specially prepared and dried, and was found to be as stated by the maker, 99.89 per cent. pure.

Ethyl Alcohol (C_2H_5OH) *in Water. Molecular Weight* 46.

N	s' Observed.	ζ
12.5	1.0509	59.8
50	1.0194	64.3
100	1.0074	59.7
200	1.0026	55.5
300	1.0009	51.2

These observations illustrate the well-known fact observed by Dupré and Page,[1] and by Schüller,[2] that the specific heat of solutions of alcohol in water is greater than that of water. The molecular heats do not show the same constancy as that exhibited by the other solutions which have been presented. They increase with the concentration up to a certain point and then again decrease.

24. *Water in Aniline.*—The aniline used was Kahlbaum's product, obtained from Eimer and Amend. Its color was a yellowish red, which rapidly deepened when it was exposed to the air and heated in the calorimeters. It was at first used as it came from the bottles, but some control experiments were made by mixing the contents of several bottles in a large flask and using the homogeneous substance thus obtained as stock. A quantity, after it had been once used, was recovered by distillation over sodium and used in the same way with similar results. My observations are not in accord with those of Griffiths,[3] who found that the specific heat did not change when the aniline changed color by exposure to the air and to heat. Certain irregularities in my observations which could be explained by supposing that the aniline which I had been using as standard had experienced a change of its specific heat led me to compare it with fresh aniline, with the result that the specific heat of the used aniline was shown to be less than that of the other by more than 0.8 of 1 per cent. In the subsequent experiments the standard aniline was renewed after each set of observations.

The specific heat of aniline was taken as 0.5175, which is the value given by Griffiths (l. c.) for 25°, about the mean between the extreme temperatures in the calorimeters. Its molecular weight, from the formula $C_6H_5(NH_2)$ is 93. In order to make the results comparable with those obtained with water as solvent, it seemed best to make up solutions which should contain about the same number of molecules of the solute in unit volume as in the previous experiments, rather than those in which the gram-molecular concentration should be the same. In general this is attained by making the gram-molecular concentration five times as great as with water.

[1] Phil. Trans., 1869, Pogg. Ann., Ergänzungsband V., p. 21.
[2] Pogg. Ann., 1871, Ergänzungsband V., p. 116.
[3] Phil. Mag., January–June, 1895, p. 47.

Water (H_2O) *in Aniline. Molecular Weight* 18.

N	s' Observed.	s' Calculated.	ζ
10	0.5425	0.5445	33.0
20	0.5310	0.5312	34.6
25	0.5292	0.5285	36.6
40	0 5242	0.5243	34.4
60	0.5223	0.5221	36.0
Mean molecular heat,			34.9

Of these observations, those for $N = 60$, and $N = 25$ were made with fresh aniline. The solutions for the others were made from the solution for $N = 60$ by adding the requisite quantities of water, and the same standard aniline was used in the observations made on them. In view of what has been said of the change in the specific heat of the standard aniline with use, it seems that special weight should be given to the observations made when the aniline was fresh, or that the other observations are subject to correction. This correction, if due to the change in the standard, would increase the molecular heats determined from them. It seems to me that a more probable value for ζ would be 36. As they stand the numbers serve well enough to support the law which is under discussion in this paper.

It is worthy of remark that the specific heat of water in aniline appears to be nearly or quite equal to 2. The molecular heat is doubled by the solution. It is possible to ascribe this to an increase in the number of degrees of freedom of the water molecule due to its dissociation, and to look on it as additional evidence in favor of the view that the physical molecules of water in its liquid state are aggregates of the chemical molecules. In the present state of our knowledge it is, however, inadmissible to do more than hazard this as a speculation. Until further research has shown how to eliminate the effect of the solvent upon the solute in determining its molecular heat, we cannot consider the molecular heat as dependent upon the condition and behavior of the solute alone. That the solvent does modify the molecular heat of the solute will appear from the observations following.

25. *Glycerine in Aniline.*—The glycerine used contained 1.94

grams of water in 100 grams. Allowance was made for this in the weighing and the specific heat of the aniline used as solvent was calculated as if the water dissolved in the aniline with the molecular heat 36. The specific heat of aniline was taken as 0.5175.

Glycerine ($C_3H_8O_3$) *in Aniline. Molecular Weight* 92.

N	s' Observed.	ζ
12.5	0.5427	76.6
24.6	0.5321	79.7
50.	0.5252	81.
100.	0.5215	83.

There seems to be a decrease of ζ as the concentration increases. In view of this and of the way in which the water contained in the glycerine was reckoned in with the aniline, I have not thought it worth while to calculate the specific heats. One thing is evident from this table, namely, that the apparent molecular heat of glycerine in aniline is not the same as it is in water. The values are about in the ratio of 80 to 54. This difference is far too large to be due to errors of observation.

26. *Urea in Ethyl Alcohol.*—The alcohol used was ordinary alcohol distilled over lime. A large quantity was mixed in a bottle and used as stock. The urea was the same product as that used with water. The specific heat of alcohol was taken as 0.6019.[1]

Urea (CON_2H_4) *in Ethyl Alcohol. Molecular Weight* 60.

N	s' Observed.	s' Calculated.	ζ
42.4	0.5984	0.5979	28.8
70.65	0.5992	0.5994	27.5
Mean molecular heat,			28.1

In this case the molecular heats are constant to within the limits of error of the observations, which were rendered more uncertain than with aqueous solutions by the greater volatility of the alcohol. The molecular heat obtained for urea is different from its value in an aqueous solution in the ratio of 28 to 21. This difference is

[1] Schüller, Pogg. Ann., Ergänzungsband V., p. 119.

again so large that I do not feel willing to ascribe it to errors of observation. If ζ were 21, as it seems to be for urea in water, the specific heat of the solution $N = 70.65$ would be 0.5973. The difference between this and the number found, 0.5992, while not large, is outside of the variations of the individual results from which the mean was determined.

Yet, while this is true, there may be some unnoticed error in the measurements which, if detected, would account for this slight difference; and I do not feel that the question will be settled without more extended investigation.

27. *Glycerine in Ethyl Alcohol.*—The glycerine was the same product as that used before. Allowance was made for its water content by adding the appropriate amount of water to the alcohol used as standard.

Glycerine ($C_3H_8O_3$) *in Ethyl Alcohol. Molecular Weight* 92.

N	s' Observed.	ζ
35.32	0.5967	46.25
70.65	0.5967	37.5
141.3	0.5975	27.0

In this case there is a variation of the molecular heat similar to that exhibited by solutions of alcohol and water.

28. It is evident that the prediction of the theory is fulfilled in very many of the solutions which have been examined. In these cases we may safely say that the conditions upon which the theory was based have also been fulfilled and we may therefore expect the depression of the freezing point to correspond with that indicated by van't Hoff's formula. This has been proved for the aqueous solutions by the recent experiments of Professor Loomis.[1] The solution of alcohol in water as measured by him does not agree precisely with the van't Hoff formula; and this may have something to do with the anomalous behavior of its specific heat. In solutions containing alcohol, either as solute or solvent, it seems as if the law of equation (g) did not hold. The anomalous behavior of alcohol in this respect was proved by Schüller for solutions of alcohol with water,

[1] Princeton University Bulletin, January, 1899.

benzene, chloroform and bisulphide of carbon, and is proved by my experiments for solutions of glycerine in alcohol, and for dilute solutions of alcohol in water. The one exception seems to be in the case of urea in alcohol. Even in this case it is not proved by my observations that the specific heat of urea in alcohol is constant. The two results obtained, for example, may lie on either side of a maximum, such as is exhibited by alcohol in water.

29. I do not feel that the results before me warrant a definite declaration as to whether or not the molecular heats obtained are independent of the solvent. On the modern theory of solutions it would seem that the specific heats, as well as the other properties of the solutes, should be those which they would exhibit in the gaseous state. The specific heats obtained for cane sugar, dextrose, glycerine, mannite and urea, dissolved in water, are not inconsistent with this view. On the other hand, the value 36 obtained for the molecular heat of water in aniline, speaks decidedly against it. The specific heat of water vapor is about 0.5, so that the heat capacity of water in solution in aniline is about 4 times as great as that of water vapor. So far as this example carries any weight, it shows that the solute is not so entirely independent of the solvent that its energy is unaffected by the solvent. The same conclusion may be drawn from the molecular heats of glycerine in aniline and of urea in alcohol, though the former of these cases may be one similar to that of alcohol in water, as indicated by the variations of the molecular heat with concentration.

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AN INTERFEROMETER STUDY OF RADIATIONS IN A MAGNETIC FIELD. II.

BY JOHN C. SHEDD.

PART TWO. THE INTERFEROMETER METHOD.

Professor Michelson[1] has shown the peculiar adaptability of the interferometer for the class of research here considered.

The instrument used in the present case was received March 1, 1898, and has proved highly satisfactory for the work undertaken.

The instrumental difficulties attending the use of the Interferometer are such as perhaps to warrant a word about them. These difficulties arise from two sources: (1) defective workmanship in the instrument, and (2) those due to the observer. These will be considered in order: (1) the most serious error that can be present is a lack of parallelism in the ways along which the mirror carriage moves. This is generally manifested by a shifting of the system of fringes in the field of view, and a more rapid loss of visibility on the part of the fringes than should take place.[2] A second defect is sometimes present in the optical quality of the glass, due either to a defective surface, or to internal stress in the glass. This defect is manifested by a distortion of the fringes which under proper adjustment should appear as circles. A third defect, easily overlooked, is in the silvering of the surfaces. The two end mirrors (see Fig. 10) M' M'' should be heavily silvered, and brightly polished. The half-silvered surface (M), however, should have such a film as will transmit and reflect equal amounts of light. If this be true,

[1] Astro. Phys. Jr., 6, p. 48, also 7, p. 131.
[2] Phil. Mag. (5), 34, p. 286.

50% of the incident light is effective in the two interfering beams, and the fringes are of maximum brightness. There is no direct method of estimating this defect, and experience is the only proper guide. (2) A very considerable amount of patience is necessary to eliminate or minimize personal errors. Fringes are often obtained which appear satisfactory, but from a lack of exact adjustment have a variable focus, are distorted, and rapidly fade out as the movable mirror recedes. If the instrument be in adjustment the fringes appear as concentric circles, and Michelson has shown [1] that if the incident light be parallel then the fringes are at infinity.[2] If, however, the light be not parallel, then the fringes are in front of the interfering surface (*M*, Fig. 10), upon it or behind it, according as Δ is greater than, equal to, or less than zero, where Δ is the difference in the paths traversed by the two beams of light. In general it may be said that the incident beam is not parallel, and hence, that the fringes recede as Δ increases. If a telescope is used to view the fringes, the focus will have to be altered slightly, and must soon be adjusted for parallel light. If, on the other hand, the naked eye is used, there is a tendency to focus the eye upon the mirror, instead of upon the fringes. Hence an observer is apt to lose sight of the fringes altogether, or to view them out of focus unless considerable care is exercised upon this point. The real work of the interferometer consists in an eye estimate of the visibility of the fringes as Δ is increased. There is a manifest liability to error in these eye estimates, unless a comparison set of fringes of known intensity is available; but the process in such a case is not only tedious [3] but adds to the amount of apparatus to be looked after. On the whole, it is more practicable, and perhaps, as reliable to depend upon the training of the eye that comes from long practice, and in testing the eye from time to time by means of comparison fringes. However, even after a correction [4] curve is obtained and applied, there is room for a considerable margin of personal error, which is, perhaps, the chief drawback to the method as a whole.

[1] Phil. Mag. (5), 13, p. 239, 1882.
[2] Except when $\Delta = 0$, when the fringes are on the mirror.
[3] Astro. Phys. Jr., 7, p. 133.
[4] Phil. Mag. (5), 34, p. 283. Such a curve is shown in Fig. 14.

Adjusting the Interferometer.[1]

The general disposition of apparatus for the present work is shown in Fig. 10.

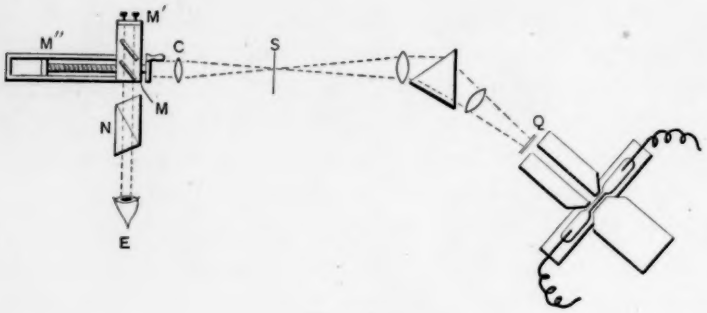

Fig. 10.

M, M', M''. Interferometer mirrors.
Q. ¼ λ plate.
N. Nicol.
S. Slit.
E. Eye or telescope.

FIRST ADJUSTMENT. *To Find the Fringes.*—The mirror *M''* is set so as to be within two or three mm. of the zero of the scale, and a Bunsen flame[2] colored with a piece of sodium glass is so set with reference to the lens *C* that the field of the mirrors is uniformly bright. Then a pin, or bit of glass fiber, is fastened by a bit of wax onto the lens, so that its image is in the center of the field. It is preferable to have the image lie obliquely across the field, not horizontally or vertically. The mirror *M'* is then adjusted until the two images of the pin, made by the two mirrors, *M'* and *M''*, are superposed. When the images lie obliquely the movements of the adjusting screws can be easily followed. When the adjustment is very close, if the room is partially darkened, and the eye focused for a point behind the mirror, the fringes should appear as fine lines covering the field. The eye should now be focused on these fringes, and

[1] The Adjustments of the Interferometer are discussed at length by Professor Wadsworth in PHYS. REV., Vol. 4, p. 480. See also p. 400 of same vol.

[2] The Bunsen flame occupies the position of slit *S* in Fig. 10, the rest of the system to the right of *S* being absent.

the screws adjusted so that the fringes grow broader and more distinct. The final adjustment is reached when they appear as concentric circles, which do not change in appearance, when the eye is shifted in any direction. Under these conditions the two mirrors, M' and M'', are optically parallel to each other.

Second Adjustment. *To Find Zero of the Instrument.*—The zero of the instrument is the position of zero difference of path between the two interfering beams of light. It is found by obtaining fringes with white light and adjusting on the central black fringe of this system. To obtain fringes with white light the mirror M' should first be adjusted so as to give the fringes as vertical lines of small curvature. If now the mirror M'' be moved back and forth by slow motion, the fringes will be seen to change curvature at one region. The exact point of this change of curvature is the point sought. Having adjusted approximately for this, a candle flame should be set before the Bunsen flame, giving the white image of the candle flame with a background of sodium fringes. The mirror M'' may now be slowly moved by means of the tangent screw, the motion being followed by the eye, in the progression of the (faint) sodium fringes. When the zero point is approached brilliant chromatic fringes, from ten to twenty in number, will appear in the image of the candle flame. If now the candle be removed, and the air cut off from the Bunsen flame the chromatic fringes are very distinct and brilliant.

The zero point will shift a little with change of temperature, and still more by a change in the distance of the mirror M' from M due to difference in the manipulation of the adjusting screws. The zero should therefore be observed before each set of observations.

Visibility Curves.

The theory of the visibility curve has been given by Michelson, and its adaptation shown to problems where the distribution of light as a source of radiation is to be determined.

The following curves were taken using sodium light as source of illumination, and viewing the light first perpendicular to the field, and than parallel to it.

I. Perpendicular to the Field. The curves taken are shown in Fig. 11, *A*, and the corresponding distribution of light in Fig. 11, *B*[1].

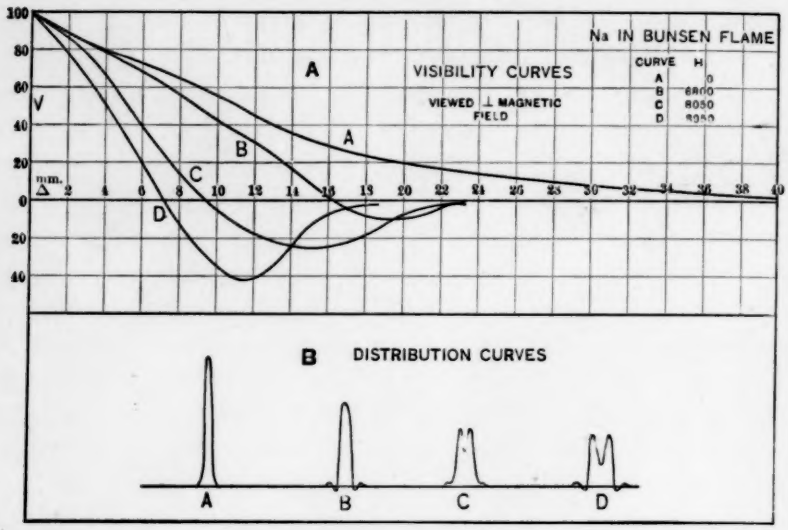

Fig. 11.

In this curve the nicol prism was not used, and the loss of light by the central component (which is known to be present), is such as to render the line an apparent double.[2] In the curves *B*, in those marked *B*, *C*, *D* the main components seem accompanied by small companions some having negative ordinates. Now since this would indicate negative intensities, they indicate errors in observing the curves *A*. The analysis of the curves *A* then furnish a valuable check upon their correctness.

II. Light Viewed Parallel to the Magnetic Field. Curves were taken for this position both with and without the nicol. The results are shown on Figs. 12 and 13. These are substantially identical and show first a broadening and then a doubling of the spectral lines. The presence of the negative ordinates is also seen and yet the substantial results are clear.

[1] Acknowledgment is due to Professor Michelson who kindly facilitated the analysis of these curves on the Harmonic Analyzer at the University of Chicago.

[2] See part I, also Michelson, Astro. Phys. Jr., 6, p. 49.

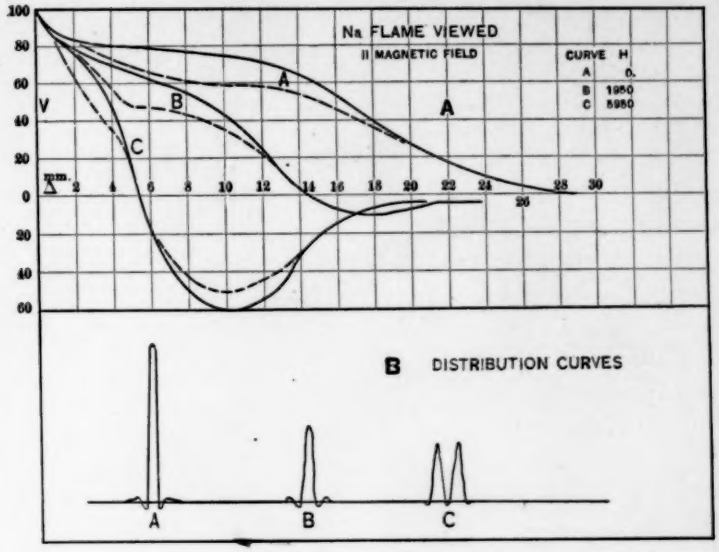
Na FLAME VIEWED
|| MAGNETIC FIELD
CURVE H
A D.
B 1950
C 5980
V
A
B
C
mm.
Δ 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
B DISTRIBUTION CURVES
A
B
C

Fig. 12.

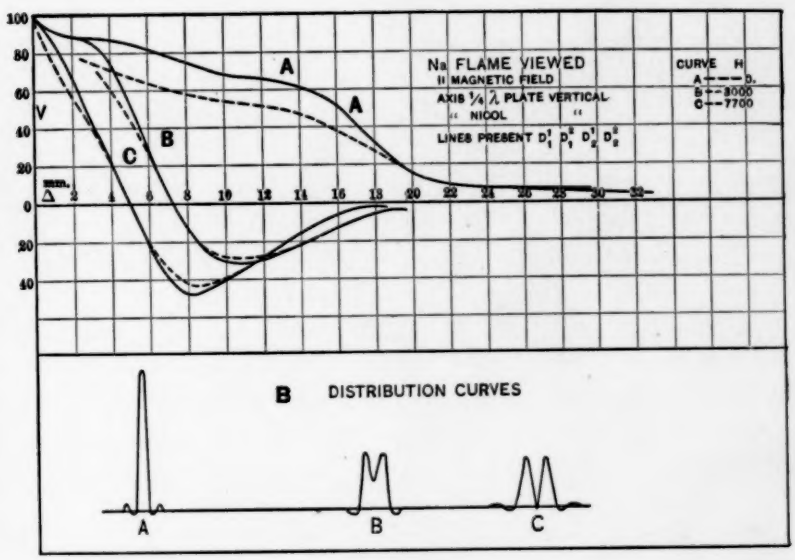
Na FLAME VIEWED
|| MAGNETIC FIELD
AXIS ¼ λ PLATE VERTICAL
" NICOL "
LINES PRESENT D_1^1 D_1^2 D_2^1 D_2^2
CURVE H
A D.
B 3000
C 7700
V
A
B
C
mm.
Δ 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32
B DISTRIBUTION CURVES
A
B
C

Fig. 13.

Having analyzed these curves a comparison curve was then taken to observe what correction was necessary to reduce the eye estimates shown in the full line curves of Figs. 11, 12 and 13. The resulting curve is shown in Fig. 14 and the corrected visibility curves are shown in the dotted curves of Figs. 12 and 13. These corrected curves were not analyzed, but their distribution curves would be more nearly correct than those shown. We have then in the curves shown all observational errors present; the result, though not satisfactory, is by no means bad. This form of error is very hard to avoid and long practice alone can eliminate it.

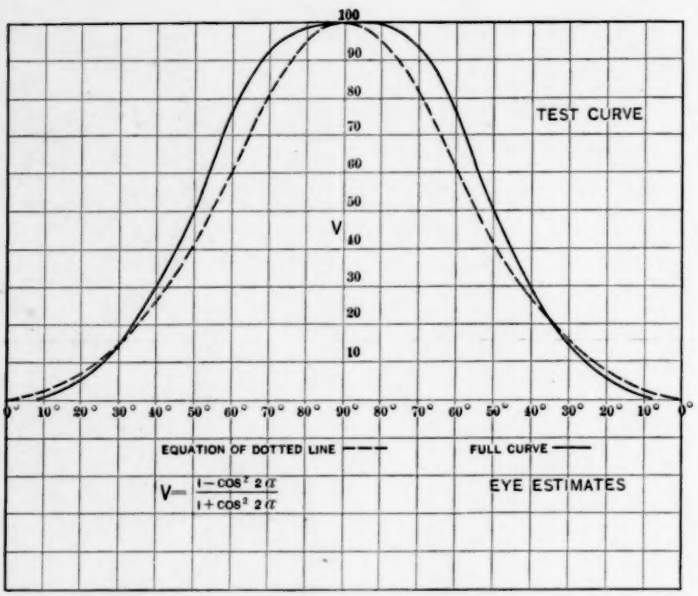

Fig. 14.

Polarization.—The interferometer was found to be capable of showing the state of polarization in the most elegant manner, not only identifying the plane of polarization, but also immediately identifying the accelerated from the retarded ray.

Thus with the axis of the $\frac{1}{4}\lambda$ plate vertical the nicol was rotated and the action and character of the fringes observed. The following were the results obtained:

TABLE II.

Position of Axis of Nicol.	Action of Fringes on Magnetization.	Character of Central Fringe with Magnetic Field.
0° Vertical.	Become hazy.	Hazy.
+ 45°	Expand and remain distinct.	Distinct, dark.
+ 90° Horizontal.	Become hazy.	Hazy.
+135°	Contract and remain distinct.	Distinct, light.
180° Vertical.	Become hazy.	Hazy.
—135°	Expand and remain distinct.	Distinct, dark
— 90° Horizontal.	Become hazy.	Hazy.
— 45°	Contract and remain distinct.	Distinct, light.
0° Vertical.	Become hazy.	Hazy.

It is evident that the haziness at $0° \pm 90°$ and 180° is due to the simultaneous contracting and expanding of the fringes. Further analysis shows us that when the fringes expand the retarded component is present and when the fringes contract the accelerated (or shorter wave-length) component is present.

This is shown in Fig. 15. Unpolarized light is represented by the superposition of the two perpendicular planes of vibration.

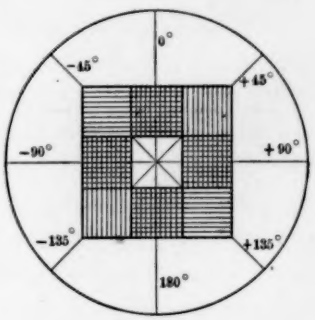

Fig. 15.
Axis of ¼ λ plate vertical, Nicol rotated.

From this general survey of the interferometer we derive the following generalizations :

1. The interferometer is capable of showing the magnetic effect for field strengths below 1,000 C. G. S.

2. The visibility curves, even under unfavorable circumstances, show clearly the general character of the magnetic effect and when checked through a long series, by means of an harmonic analyzer, furnish an incomparable method of analysis.

3. When unaccompanied by such a check errors are not readily eliminated and for quantitative measurements of change in wave-length another use of the interferometer furnishes a better method.

Inasmuch as the visibility curve analysis was, not under the circumstances, entirely available, attention was turned to the development of point 3 above and carried out as follows :

Measurements of Change of Wave-length.

Method.—Professor Michelson[1] in determining the difference in wave-length between the components of the magnetic line makes use of what he calls the "period of coincidence due to doubling." This may be defined as follows: Consider two systems of fringes produced by light sources differing but little in wave-length. Then the *resultant* system due to both sources, will be the resultant of the overlapping of the component systems, and at certain points destructive interference will take place, and at others reinforcement. The fringes will then run through a series of maxima and minima as $\triangle$ is increased. The distance from maximum to maximum is the "period." If $\triangle$ be measured from "zero" to the first point of reinforcement, then the following equation holds

$$\triangle_p = N\lambda = (N+1)\,\lambda' \qquad (11)$$

where N is the total number of fringes; and $\triangle$ and λ are measured in mm. In the case of the lines D_1 D_2 these maxima occur every 988 fringes and $\triangle_p = 0.58242$ mm. In the case, however, of the magnetic shift the difference of wave-length is so small that Michelson finds the values of $\triangle$ to range from 58 mm. to 14 mm. as the magnetic field increases to 4,000 C. G. S. units. The same method is also described by Perot and Fabry[2] and is especially applicable where the difference of wave-length is sufficient to give a difference of color to the two sets of fringes.

When applied to the magnetic components the method is open to improvement. In the first place the fringes, at a point where $\triangle =$ 50, or even 30, are so narrow and frequently so faint that an accurate determination of points of reinforcement (*i. e.*, where both systems agree in phase) is not easy. Secondly, since the magnetized and unmagnetized fringes cannot be simultaneously observed, the above determination consists in finding the value of $\triangle$ at which the closing of the magnet shifts the system the double width of one fringe. This determination for high values of $\triangle$ is not as easy as might be wished.

[1] Astro. Phys. Jr., 6, p. 50.
[2] Astro. Phys. Jr., Feb., 1899. See Appendix III.

There are, however, two possible modifications. If the nicol be not used, it has been seen that the magnetized components draw apart, one being retarded and the other accelerated. The corresponding effect on the fringes is to cause the original system simultaneously to contract and expand. If now the point is found at which the two systems of fringes are tangent to each other, each fringe will have shifted ½ its own width, showing that the accelerated system is ½ period in advance of the retarded one, or ¼ period removed from the original system. We then have the equation

$$\triangle_{\frac{1}{4}P} = N\lambda = (N + \tfrac{1}{4})\lambda'. \qquad (12)$$

The second modification consists in using the nicol and in thus quenching one of the component systems. Now concentrate the attention upon one fringe, either adjusting a pointer (fastened to lens *c*, Fig. 10) to its edge, setting the fringe tangent to a line drawn on the mirror *M*, or by merely observing the central fringe of the system. Let it be supposed that the central fringe is dark, and the field unmagnetized. On turning on the current the system contracts, and for a certain value of $\triangle$ will be the exact complement of the first, the center being now light instead of dark.

Under these conditions the fringes have shifted over their own width, and the following equation is obtained.

$$\triangle_{\frac{1}{2}P} = N\lambda = (N + \tfrac{1}{2})\lambda'. \qquad (13)$$

Still a third modification would be as follows: Let the field remain magnetized and set the fringe, with the nicol in a given position, tangent to the fixed line. Then let the nicol be rotated 90°, so as to bring the other system of fringes into view; then that value of $\triangle$ which renders the line a common tangent to both systems gives a difference of period such that

$$\triangle = N\lambda_1 = (N + 1)\lambda_2$$

where λ_1 and λ_2 are the component lines. Also since λ_1 and λ_2 lie symmetrically with respect to λ (the unmagnetized line) we have

$$\triangle = N\lambda_1 = (N + \tfrac{1}{2})\,\lambda = (N + 1)\,\lambda_2$$

or, putting the equation in terms of λ,

$$\Delta = N\lambda = (N \pm \tfrac{1}{2})\lambda' \qquad (14)$$

which is identical with equation (13).

Since in the above equations N is the total number of fringes passed over from the position $\Delta = 0$, some means must be had of knowing its value. This is obtained very simply as follows: If λ be given in mm. then $1/\lambda$ equals the number of fringes per mm., and $N = \Delta/\lambda$, Δ being measured in mm. Substituting this value in the above equations and solving for $\lambda - \lambda'$, the following equations are obtained

$$\left.\begin{aligned}
&\text{For } \Delta_p \text{ equation } (11)\\
&\qquad \lambda - \lambda' = \frac{\lambda\lambda'}{\Delta} = \frac{\lambda^2}{\Delta} \qquad (11')\\
&\text{For } \Delta_{\frac{1}{4}p} \text{ equation } (12)\\
&\qquad \lambda - \lambda' = \frac{\lambda\lambda'}{4\Delta} = \frac{\lambda^2}{4\Delta} \qquad (12')\\
&\text{For } \Delta_{\frac{1}{2}p} \text{ equation } (13)\\
&\qquad \lambda - \lambda' = \frac{\lambda\lambda'}{2\Delta} = \frac{\lambda^2}{2\Delta} \qquad (13')
\end{aligned}\right\} \qquad (15)$$

For a given, value of $\lambda - \lambda'$ we have the relation

$$\Delta_p = 4\Delta_{\frac{1}{4}p} = 2\Delta_{\frac{1}{2}p}. \qquad (16)$$

This last equation would indicate that the second method given by equation (12′) would be the most accurate since it gives the smallest values of Δ and hence the widest and brightest fringes. It must, however, be noticed that the condition expressed by equation (12) is that the two systems of fringes shall differ by $\frac{1}{2}$ period and hence that the dark rings of one system shall coincide with the light rings of the other. Hence the field will be uniformly illuminated and the fringes disappear. In practice there is found to be a region over which the fringes are blurred and the exact point of extinction is difficult to determine.

On the other hand, in the third method the fringes are always sharp and for values of H above 2,000 C. G. S. units the values of Δ are small enough to render the fringes sufficiently wide for satisfactory observation.

With a little practice the method of observing the central fringe was found to give concordant readings and hence was used in preference to setting the fringe tangent to a line.

A comparison of the three methods is given by equation (16). Still further light is given by substituting the value of $\frac{\lambda-\lambda'}{\lambda^2}$ from equations (13) in equations (9).

Making this substitution we get

$$\left.\begin{array}{lll} \text{1st method.} & H\triangle = 4\pi v\frac{m}{e}\cdots(11'') \\ \text{2d} \quad " & H\triangle = \pi v\frac{m}{e}\cdots(12'') \\ \text{3d} \quad " & H\triangle = 2\pi v\frac{m}{e}\cdots(13'') \end{array}\right\} \qquad (17)$$

If m/e be regarded as constant, these equations all represent rectangular hyperbolæ asymptotic to H and $\triangle$ taken as axes.

It is thus seen that curves expressing the relation of H and $\triangle$ furnish a ready means of comparison both by equations (16), and by their form as indicated by equations (17). Such a set of comparison curves was taken with an oxygen gas flame colored with sodium. In Table III. the values of $H\triangle$ for different parts of the curve are given, and the curves themselves are given in Fig. 16.

TABLE III.

Method II.			Method III.		Method I.	
H[1]	$\triangle$	$H\triangle$ (curve A.)	$\triangle$	$H\triangle$ (curve B.)	$\triangle$	$H\triangle$ (curve C.)
2,300	15.4	354	21.4	492	13.1	300
3,000	12.0	360	16.7	500	12.0	360
4,000	9.0	360	13.3	530	11.0	440
5,000	7.3	365	10.5	526	10.0	500
6,000	6.2	370	8.2	490	9.0	540
7,000	5.5	385	6.8	475	8.2	575
8,000	4.8	384	5.8	465	7.4	590
9,000	4.3	386	5.2	470	6.7	602
10,000	3.8	380	4.8	480	6.1	610
11,000	3.5	386	4.5	496	5.6	615
12,000	3.4	408	4.4	528	5.3	635

[1] H throughout these experiments was determined by the balistic method.

Curves *A* and *B* corresponding to Methods II. and III. show a close correspondence with equation (17) while curve *C* is manifestly unreliable.

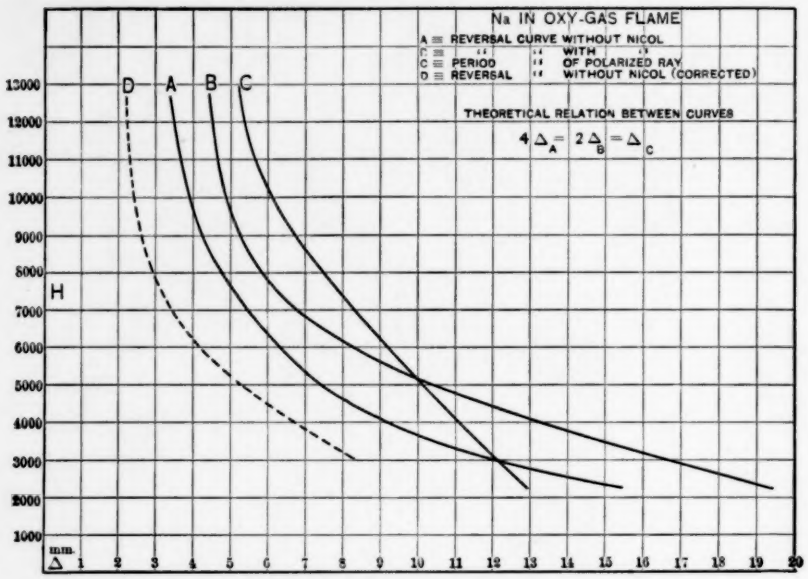

Fig 16.

Comparing curves *A* and *B* we see that equation (16) is not fulfilled, and hence that either one or both curves are displaced. From the fact already pointed out as to the difficulty of making settings for curve *A* we have no hesitation in concluding that the readings for this cure are uniformly too high.[1] Assuming that curve *B* is correct, the dotted curve *D* gives the corresponding position for curve *A*.

SECTION III. COMPARISON OF MAGNETIC SHIFT AT DIFFERENT TEMPERATURES.

To investigate this the sodium flame was used and *reversal* curves taken, by Method III., under the following conditions: I. Bunsen flame, II. Oxy-gas flame, III. Vacuum tube.

[1] It is not to be supposed that curve *A* represents the greatest accuracy attainable by Method II. Continued observation would undoubtedly render this method quite available.

The light was viewed parallel to the magnetic field as giving the most uniform structure of line (see Fig. 3, *B*), and a $\frac{1}{4}\lambda$ mica plate used. The following tables are selected as representative.

TABLE IV.

Reversal Curves. Na in Bunsen Flame.

H C. G. S. units.	Δ mm.	λ—λ′ A. U.
0,000	∞	0.000
3,000	12.80	0.135
4,000	11.65	0.155
5,000	10.60	0.168
6,000	9.60	0.180
7,000	8.50	0.205
8,000	7.70	0.230
9,000	6.40	0.274
9,500	5.40	0.325
9,600	5.00	0.350
9,700	4.90	0.370
9,800	4.80	0.375
10,000	4.70	0.380
11,000	4.65	0.380
12,000	4.65	0.380
13,000	4.65	0.380

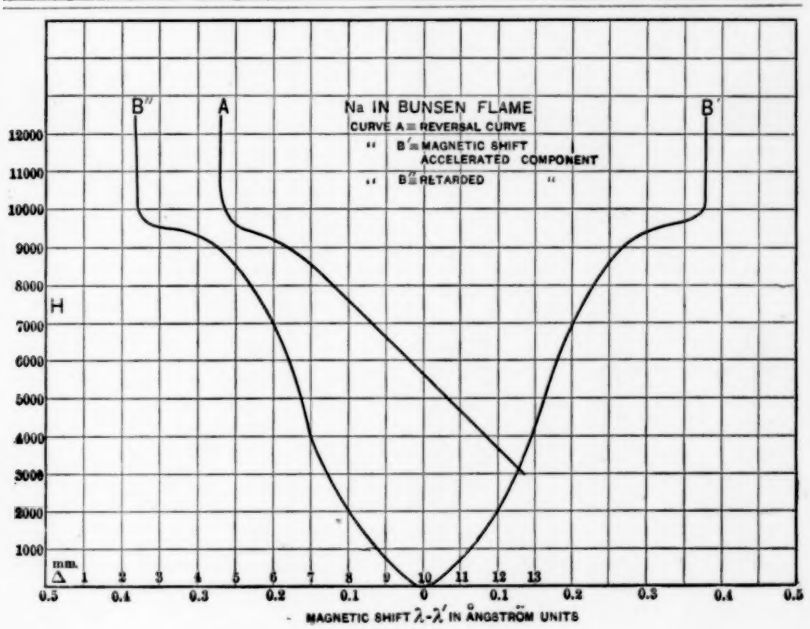

Fig. 17

Table IV. is platted in Fig. 17. The part of the curve lying between 8,000 C. G. S. and 11,000 was checked up with special care and the knee in the curve verified. For all readings where Δ is less than 3 mm. a small change in Δ indicates a large change in $\lambda - \lambda'$, and hence the readings become less sensitive. The departure of the reversal curve from the normal hyperbolic form would indicate, as is shown in curve *B*, Fig. 17, an ionic inertia or lag, due either to low temperature or high density of the gas, or to both This constraint retards the change in wave-length but suddenly gives way at a field strength of about 9,500. Above a value of *H*, of 10,000 the mean wave-length of the lines do not seem further to change, increase in *H* beyond this point being effective in broadening the lines rather than in separating them.

In curves *A* and *B* (Fig. 18) a small flame 2 cm. high was used with the tip of the inner cone opposite the aperture. In curve *C* the jet was 15 cm. high and the base of the flame opposite the opening. The flame in both cases was colored with a bead of fused sodium carbonate.

Curve *C* shows the same "lag" as does the Bunsen flame, and the maximum value of $\lambda - \lambda'$ is not so large. In curves *A* and *B*,

TABLE V. See Fig. 18.

Reversal Curves. Na in Oxygen-gas Flame.

H	Δ_A mm.	Δ_B mm.	Δ_C mm.	$(\lambda-\lambda')_A$	$(\lambda-\lambda')_B$	$(\lambda+\lambda')_C$
0	∞	∞	∞	0.000	0.000	0.000
2,500	17.20	18.50	19.40	0.105	0.097	0.090
3,000	16.00	17.15	18.00	0.111	0.105	0.100
4,000	13.30	14.35	15.35	0.135	0.125	0.115
5,000	10.80	11.70	12.80	0.164	0.151	0.140
6,000	8.25	9.00	10.70	0.212	0.197	0.165
7,000	6.20	6.95	9.10	0.285	0.251	0.197
8,000	5.10	5.80	7.80	0.345	0.304	0.228
9,000	4.55	5.10	6.90	0.390	0.345	0.254
9,500	4.40	4.90	6.50	0.400	0.360	0.275
10,000	4.30	4.70	6.00	0.410	0.375	0.310
10,500	4.25	4.50	5.40	0.420	0.402	0.334
11,000	4.15	4.40	5.15	0.430	0.402	0.345
12,000	4.05	4.40	5.10	0.442	0.402	0.345
12,700	4.00	4.40	5.10	0.442	0.402	0.345

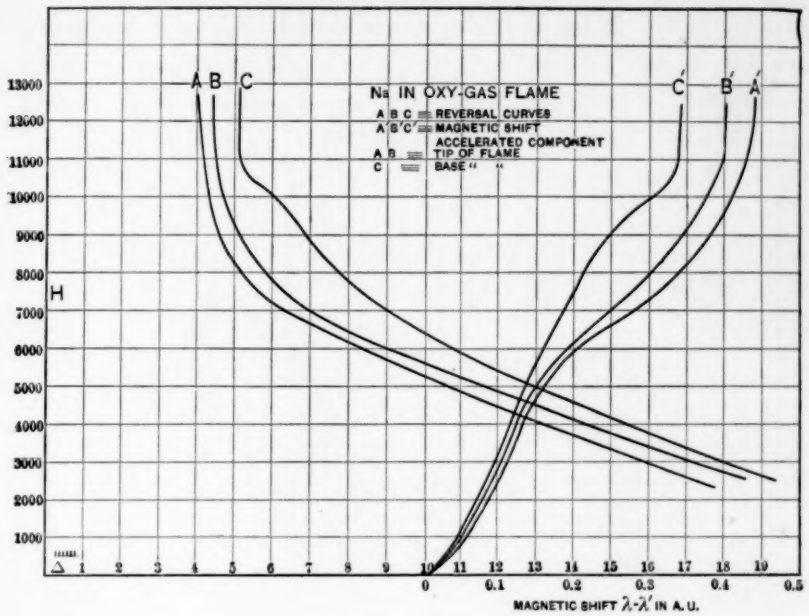

Fig. 18.

which are at a higher temperature, this lag is overcome at a lower value of H, and the maximum value of $\lambda - \lambda'$ is larger.

TABLE VI. See Fig. 19.

Reversal Curve. Na in Vacuum Tube.

H	Δ mm.	$\lambda - \lambda'$ A. U.
0	∞	0.000
5,000	11.20	0.160
6,000	9.50	0.186
7,000	7.90	0.225
8,000	6.30	0.280
9,000	5.00	0.352
9,500	4.60	0.384
10,000	4.25	0.415
10,500	4.10	0.431
11,000	4.00	0.441
12,000	4.00	0.441
13,000	4.00	0.441

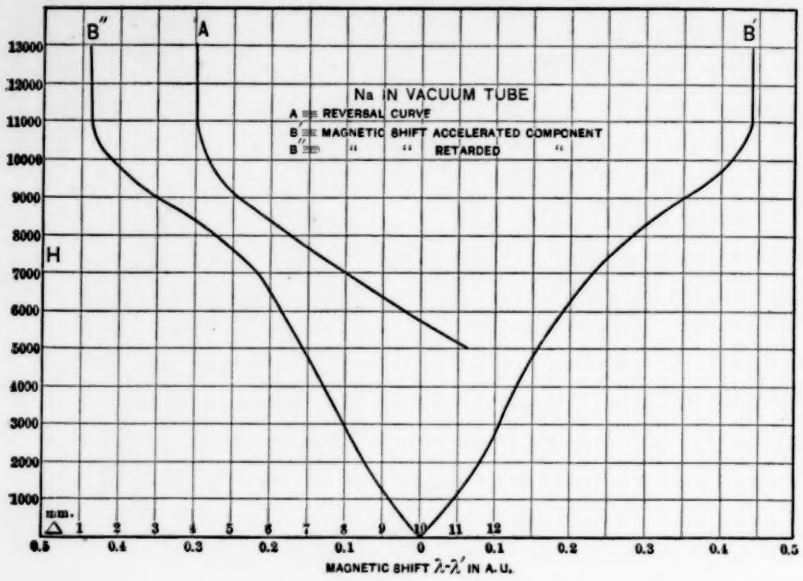

Fig. 19.

Fig. 19 would seem to show that at the temperature of the vacuum tube the change of $\lambda - \lambda'$ is nearly proportional to H up to 7,000 C. G. S., at which point the "lag" is overcome. At 11,000 the maximum for $\lambda - \lambda'$ is reached.

In the case of the vacuum tube, the tube was arranged as shown in Fig. 20. The brass tube T is made to fit over the pole heads of the magnet, and is capped at either end, thus forming a metal box. Into this box the vacuum tube is placed, being held from contact with the metal by asbestos wool.

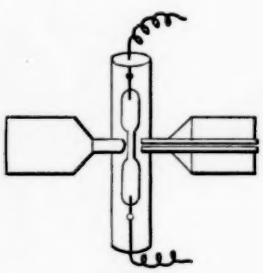

Fig. 20.

A Bunsen flame is so supported as to play horizontally upon the tube. Small glass tubes enter the caps and convey wires to the terminals of the vacuum tube which was energized by an induction coil of the usual type. The substance whose spectrum was to be examined was placed in the tube, in the form of filings, and the tube then exhausted to between 1 mm. and 2 mm. pressure. The brass tube was then heated by means of the

Bunsen flame, until the spectral lines appeared sharp and bright. In some cases the heating was pushed too far, resulting in chemical action on the glass.

Upon using the vacuum tubes it was found that the glass of the tube itself acted as a retardation plate, adding its effect to that of the $\frac{1}{4}\ \lambda$ mica plate. It was thus found impossible to produce an exact retardation of $\frac{1}{4}$ period. With reversed positions of the nicol prism, however, the two systems of fringes were found to be clear and sharp so that the arrangement was satisfactory if not ideal. The mica plate was used part of the time, and part of the time discarded.

In the preceding curves the effect of pressure cannot be separated from the temperature effect. The combined effect is what is observed. An interesting detail yet to be studied is the case where the pressure is gradually varied, and a pressure curve obtained.

Summary.—From a study of these curves we draw the following conclusions with regard to the effect of temperature.

I. At the temperature of the Bunsen flame there is a distinct ionic "lag" or constraint which is overcome, suddenly, at a field strength of 9,500 C. G. S. units.

II. This ionic lag becomes less as the temperature rises and is practically absent at the hottest temperature of the oxygen-gas flame or of the vacuum tube.

III. The change in wave-length reaches a maximum value depending upon the temperature (and pressure); the maximum is reached at about 11,000 C. G. S. For values of H above this the magnetic effect is to broaden the lines and not to separate them further.[1]

This latter point receives support from Michelson's echelon spectroscope which shows the sodium lines to belong to type II. (See Fig. 3, *B*.

NOTE. An attempt was made to take observations with the spark gap. A glass tube 1 mm. bore was taken, and metallic sodium crowded into it until 2 or 3 cm. of the tube at the center was filled. The tube was then cut at the middle of the sodium, and the free ends used as spark terminals.

On turning on the magnet the electro-dynamic action of the field caused a spark to fan out showing in a very pretty manner the magnetic equipotential surfaces. This has also been observed by M. Cornu. (Astro. Phys. Jr., 7, p. 166, note 2.)

[1] This may be peculiar to the sodium lines, and be due to the simultaneous presence of the lines D_1 and D_2. No observations have yet been made upon them separately, the dispersion necessary to isolate them being too great.

SECTION IV. MEASUREMENTS OF MAGNETIC SHIFT.

Equation (9) may be put into the form

$$\lambda - \lambda' = \left(e/m \frac{\lambda^2}{4\pi v}\right) H \qquad (18)$$

showing that for a given value of λ the change in wave-length should be proportional to H provided no constraint is present. We have seen that in the case of sodium (and presumably for all substances) a constraint is present at low temperatures, but that it disappears as the temperature rises. In the measurement of magnetic shift it is important that the temperature be high, and, preferably, that the pressure be low. These conditions are fulfilled by the vacuum tube; hence it was used as a source of illumination.

It was primarily intended to make an extended series of observations upon the spectral lines of different substances, but the difficulties encountered of breaking tubes, deposits in the capillary, and chemical action within the tube, were such as to reduce the number of satisfactory observations to sodium, zinc, mercury and cadmium. Difficulty was also met with in getting readings upon lines lying near either end of the visible spectrum.

The following are the data taken:

Sodium. *Yellow lines* ($D_1 D_2$).—The probable linear relation of $\lambda - \lambda'$ to H can be derived from Fig. 21, curve B, by drawing a line from the origin tangent to the curve. This is given in Fig. 24.

Zinc. *Blue line.* $\lambda = 4810.724$. (For arrangement of apparatus, see Fig. 10.)

TABLE VII.

H. C. G. S.	Δ mm.	$H \times \Delta$
4,000	10.2	408
5,000	8.30	415
6,000	6.80	408
7,000	5.80	406
8,000	5.05	404
9,000	4.40	396
9,500	4.15	394
10,000	3.95	395
10,500	3.85	405

Aver. = 403.

The average of column three is the product of $H \times \Delta$ of the equivalent hyperbola, and this, divided by any given value of H, gives a corrected value for Δ, which may be used in determining the value of $\lambda - \lambda'$. In this way a double check is secured, first, in drawing a smooth curve through the original data, and thus getting the readings of column two; and second, in "averaging" these readings in the manner shown.

In Table VII. the average of column three is 403; the value of Δ corresponding to $H = 5{,}000$, is 8.06, and $\lambda - \lambda'$ is 0.144 A. U. This is given in Fig. 21.

Mercury.—Readings were obtained on the yellow, green and violet lines as follows:

TABLE VIII.

H	Yellow line. $\lambda = 5790.49$.		Green line. $\lambda = 5460.97$.		Violet line. $\lambda = 4358.56$.	
	Δ	$H\Delta$	Δ	$H\Delta$	Δ	$H\Delta$
3,000	20	600	. .	. .	. .	. .
4,000	15.	600	12.0	480	. .	. .
5,000	11.9	595	9.5	475	. .	. .
6,000	9.85	591	8.0	480	. .	.
7,000	8.25	578	6.8	476	5.7	399
8,000	7.00	560	5.8	464	4.8	384
9,000	6.20	558	5.2	468	4.3	387
10,000	5.70	570	4.8	480	3.8	380
11,000	5.45	560	4.7	517	3.5	385
	Aver. = 579.		Aver. = 480.		Aver. = 387.	

The magnetic shift for $H = 5{,}000$ is, yellow line 0.128 A. U., green line, 0.155 A. U., violet line 0.120 A. U.

Lines are then drawn through zero and this value, thus giving the magnetic shift for any value of Δ. This is done on Fig. 22.

Cadmium.—Readings were taken on the red, green and blue lines as shown in Table IX., and platted on Fig. 23.

TABLE IX.

H	Red line. $\lambda = 6438.9$.		Green line. $\lambda = 5086.3$.		Blue line. $\lambda = 4800$.	
	Δ	$H \times \Delta$	Δ	$H \times \Delta$	Δ	$H \times \Delta$
3,000	.	. .	15.8	475	13.9	418
4,000	18.6	745	13.	520	10.7	432
5,000	14.15	708	10.8	540	8.4	420
6,000	11.4	685	9.	540	6.85	411
7,000	9.8	685	7.8	546	5.9	413
8,000	8.75	700	7.	560	5.3	424
9,000	8.	720	6.6	594	. .	. .
	Aver. = 707.		Aver. = 539.		Aver. = 420.	

The magnetic shift for $H = 5{,}000$ is red line, 0,131 A. U.; green line, 0.120 A. U.; blue line, 0.137 A. U.

The results may be summarized as follows :

TABLE X.

Substance.	Line.	Magnetic Shift for $H = 5000$	Magnetic Shift for $H = 10{,}000$
		A. U.	A. U.
Sodium.[1]	Yellow line D_1.	0.207	0.414
Mercury.	Yellow line.	0.128	0.256
"	Green "	0.155	0.310
"	Violet "	0.120	0.240
Cadmium.	Red "	0.131	0.262
"	Green "	0.120	0.240
"	Blue "	0.137	0.274
Zinc.	Blue "	0.144	0.288

This table is shown graphically on Fig. 24.

[1] The echelon shows that the separation of the components of D_2 to be about two-thirds of that of D_1. The value here found belongs to D_1, the line having the greater magnetic shift.

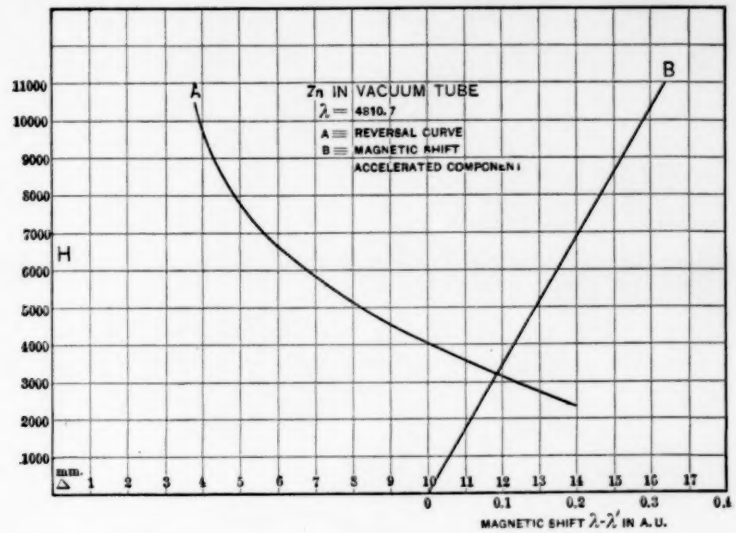
Zn IN VACUUM TUBE
λ = 4810.7
A ≡ REVERSAL CURVE
B ≡ MAGNETIC SHIFT ACCELERATED COMPONENT
A
B
H
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
mm. Δ 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
0 0.1 0.2 0.3 0.4
MAGNETIC SHIFT λ-λ′ IN A.U.

Fig. 21.

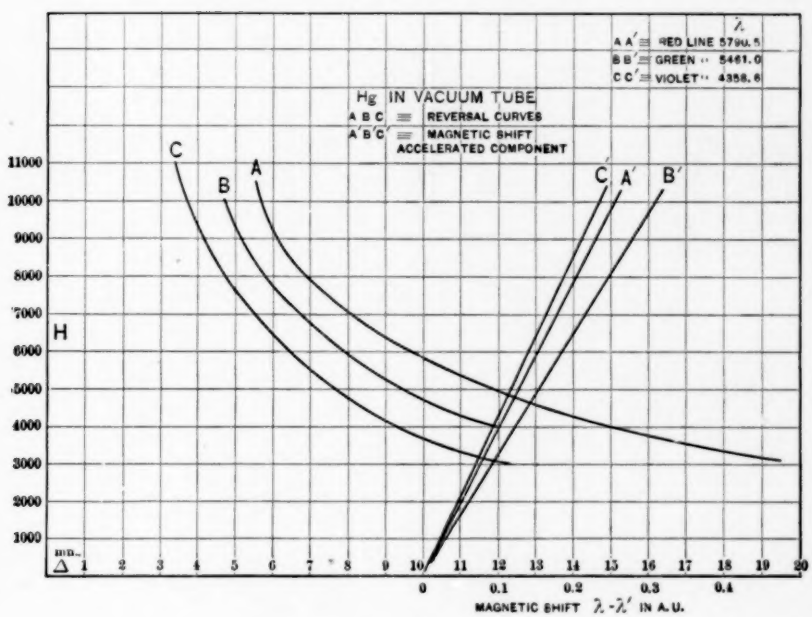
λ
A A′ ≡ RED LINE 5790.5
B B′ ≡ GREEN " 5461.0
C C′ ≡ VIOLET " 4358.6
Hg IN VACUUM TUBE
A B C ≡ REVERSAL CURVES
A′ B′ C′ ≡ MAGNETIC SHIFT ACCELERATED COMPONENT
C
B
A
C′
A′
B′
H
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
mm. Δ 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
0 0.1 0.2 0.3 0.4
MAGNETIC SHIFT λ-λ′ IN A.U.

Fig. 22.

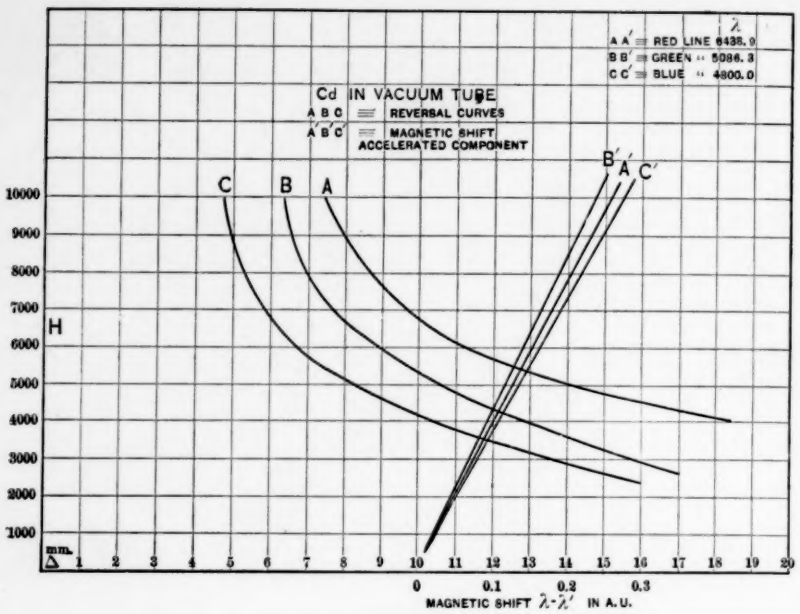
λ
A A′ = RED LINE 6438.0
B B′ = GREEN " 5086.3
C C′ = BLUE " 4800.0
Cd IN VACUUM TUBE
A B C = REVERSAL CURVES
A′ B′ C′ = MAGNETIC SHIFT ACCELERATED COMPONENT
C B A B′ A′ C′
H
10000 9000 8000 7000 6000 5000 4000 3000 2000 1000
mm. Δ 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
0 0.1 0.2 0.3
MAGNETIC SHIFT λ-λ′ IN A.U.

Fig. 23.

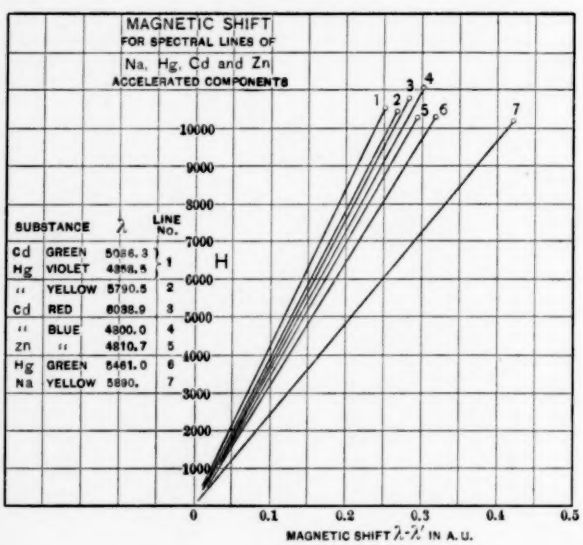
MAGNETIC SHIFT
FOR SPECTRAL LINES OF
Na. Hg. Cd and Zn
ACCELERATED COMPONENTS
SUBSTANCE λ LINE No.
Cd GREEN 5086.3 1
Hg VIOLET 4358.5 1
" YELLOW 5790.5 2
Cd RED 6038.9 3
" BLUE 4800.0 4
Zn " 4810.7 5
Hg GREEN 5461.0 6
Na YELLOW 5890. 7
1 2 3 4 5 6 7
H
10000 9000 8000 7000 6000 5000 4000 3000 2000 1000
0 0.1 0.2 0.3 0.4 0.5
MAGNETIC SHIFT λ-λ′ IN A.U.

Fig. 24.

RATIO OF IONIC CHARGE TO IONIC MASS.

Equation (10) gives the relation

$$e/m = \frac{\lambda - \lambda'}{\lambda^2} \frac{4\pi v}{H} \qquad (10)$$

for the case of circularly polarized light. This must be slightly modified for plane polarized light as the period of single vibration will be half that of the complete vibration of the circularly rotating ion. Equation (10) will then be written

$$e/m = \frac{\lambda - \lambda'}{\lambda^2} \frac{2\pi v}{H} . \qquad (19)$$

The numerical value in electromagnetic units may now be calculated from the values of $\lambda - \lambda'$ and H.

For the lines so far examined the values are as follows: The lines may be grouped according to the value of e/m; this gives the following interesting table.

TABLE XI.

Substance.	Line.	e/m	Type of line. (Michelson.)
Sodium.	Yellow.	22.45×10^5	Type II.
Mercury.	Violet.	23.81 "	
Cadmium.	Blue.	22.41 "	
Zinc.	Blue.	23.46 "	
Mercury.	Green.	18.59 "	Type III.
Cadmium.	Green.	17.48 "	
Mercury.	Yellow.	14.35 "	Type I.
Cadmium.	Red.	11.93 "	

It is thus seen that the groupings according to Michelson's chart (see Fig. 3) and according to the value of e/m are the same.

The data furnished by Preston[1] are too meager to furnish a just comparison, but it is to be said that his classification is not so well defined as is that furnished by the interferometer.

Polarization.—The method of observing the state of polarization has been outlined. In the lines examined the state of polarization

[1] Phil. Mag. (5), 45, p. 330. See part I.

was found to be normal with the exception of two cases, that seem deserving of notice.

I. *Violet Line of Mercury.*—In the readings of Table VIII. the settings were taken successively on the yellow, green and violet lines for the same value of H, by shifting the slit S in Fig. 10. The nicol was so set as to cause the fringes to expand, thus giving the retarded component. For high values of $\triangle$ the behavior of the fringes in the case of faint lines is not readily observed, and it was not until the value $\triangle = 5.14$ mm. was reached that it was noticed that the violet line contracted, while the yellow and green lines expanded. This behavior was carefully observed for the balance of the readings and persisted throughout. This peculiar state of polarization would indicate that the component of the violet line which *agrees* in rotation with the magnetic whirl is retarded instead of accelerated, as in the other lines. Hence we must have present a species of *diamagnetic* ion in contrast to the ordinary or "magnetic" ion. The above observations were taken with the greatest of care, and yet the conclusion seemed so unusual as to call for repeated verification. All attempts, however, to secure the same observations proved unavailing so far as reversed polarization was concerned.

II. In the case of the cadmium lines the following observations were made: The *red*, *green* and *blue* lines were examined, the nicol being set so as to cause the fringes to contract, thus giving the accelerated ray. The observations were begun with $H = 2{,}900$ C. G. S. units. At the second reading with $H = 6{,}600$ the fringes *all* expanded, and so also for $H = 7{,}900$. At the last reading with $H = 8{,}800$ *all* the fringes again contracted. The apparent conclusion to be drawn is that a reversal of the state of polarization takes place during the progress of the experiment. It is more likely, however, that in this case, since (as already stated) the glass of the vacuum tube acts as a retardation plate, some change of stress due either to variation in temperature or to the magnetic field, is responsible for the observed effect. This fact, in connection with the difference in wave-length between the violet and the green and yellow lines of mercury, may, perhaps, also explain the unusual behavior observed in this line. Both these cases illustrate the necessity of carefully watching the *instrumental factors* present.

Summary.—The study of the magnetic shift and the values of e/m lead to the following conclusions :

I. A classification of lines according to the amount of magnetic shift is of little value.

II. A classification of lines according to the value of e/m is significant.

III. Such a classification groups the lines according to the type of line produced, as given by the analysis of visibility curves.

IV. The smaller the value of e/m the less the broadening of the component lines and the simpler their structure; *vice versa* the larger the value of e/m the more the broadening, and the more complex their structure.

Recapitulation.

In the preceding pages the history of the subject has been traced, from the first experiments of Faraday to the present time. The bearing of the Maxwell-Lorentz theory upon the progress of Zeeman's experiments is noted, and the reacting influence of experiment upon theory is shown, so that in the papers of Larmor, Lorentz and others the mathematical exposition of the subject has kept pace with the experimental observations. In the experimental development of the problem two well-marked methods have been presented and compared. It has been found that the spectro-photographic method is (1) limited in range by reason of the small resolving power of the ruled grating when so minute changes are to be measured; and (2) is limited in accuracy by reason of the wide margin of error in the settings of the micrometer, especially when nebulous lines are to be measured.

On the other hand, the interferometer method has been seen to possess a resolving power greatly in excess of the photographic method, and hence is applicable to low values of H as well as to high values.

The results accomplished so far consist in

I. By the spectro-photographic method.

(1) A classification of lines according to the type of line produced by the magnetic field.

(2) The measurement of the distance between outside components of magnetic triplets and a determination of the value of the ratio e/m.

The number of lines so far examined is not large, nor do the values of the magnetic shift obtained by different observers seem to agree very well; but enough has been done to suggest a classification of lines parallel to that obtained by Kayser and Runge.

II. With the interferometer Professor Michelson has presented,

(1) Three well-marked types of lines, with a possible fourth type.

(2) He has concluded that the magnetic shift is to be regarded as approximately independent of substance or color.

The chief value to be attached to his work is contained in (1), and it would seem to us better to leave (2) unformulated rather than to state it as an approximate law.

The experiments described in this paper have sought to determine,

(1) The relation, at different temperatures, of the magnetic shift to strength of field.

(2) To present a method of measuring the magnetic shift that shall be as free as possible from objections involved in existing methods.

The method adopted is similar to existing interferometer methods, but is believed to be especially adapted to the present problem.

(3) To measure the magnetic shift and determine the ratio e/m.

The values obtained for magnetic shift show that any classification based upon this alone is of relatively small value; but that a classification based upon the value of e/m is significant.

This classification is seen to give groups of lines identical with the groups presented by Michelson's three types of lines.

The complexity of structure is also seen to depend upon the value of this ratio e/m.

The preceding experiments were carried on in connection with the Fellowship in Physics from 1897 to 1899 at the University of Wisconsin, under the direction of Professor Benjamin W. Snow; whom, in conclusion, I desire to thank for his helpful and continued encouragement throughout the progress of this investigation.

PHYSICAL LABORATORY, UNIVERSITY OF WISCONSIN, April, 1899.

Appendix I.

Extract from Life of Faraday by Dr. Bence Jones, Vol. II., p. 44.

"1862 was the last year of experimental research; Steinheil's apparatus for producing the spectrum of different substances gave a new method, by which the action of magnetic poles upon light could be tried. In January he made himself familiar with the apparatus, and then he tried the action of the great magnet on the spectrum of NaCl, BaCl, StCl and LiCl.

"On March 12 he writes:

"'Apparatus as on last day (January) but only ten pairs of voltaic battery for the electromagnet.

"'The colorless gas flame ascended between the poles of the magnet, and the salts of sodium, lithium, etc., were used to give color. A Nicol's polarizer was placed just before the intense magnetic field, and an analyzer at the other extreme of the apparatus. Then the electromagnet was made, and unmade, but not the slightest trace of effect on or change in the lines of the spectrum was observed in any position of polarizer or analyzer.

"'The other pierced poles were adjusted at the magnet, the colored flame established between them, and only that ray taken up by the optic apparatus which came to it along the axis of the poles, *i. e.*, in the magnetic axis or line of magnetic force.

"'Then the electromagnet was excited and rendered neutral, but not the slightest effect on the polarized or unpolarized ray was observed.'

"This was the last experimental research that Faraday made."

II.

Extract from M. Ch. Fievez (Astronome a l'Observatoire Royale de Bruxelles), *Bulletins de l'Academie Royale de Belgique*, 3d serie, tome ix., p. 381 (1885).

"L'installation spectroscopique de l'Observatoire, disposant d'un appareil dispersif de tres grande puissance et d'un electro-aimant Faraday, construction Ruhmkorff, pouvant etre active par un courant de 50 ampres d'intensite, a permis d'aborder ce probleme.

"La flamme oxyhydrique d'un petit chalumeau etait dirigee horizontalement sur un charbon *sode* place entre les armatures coniques de l'electro-aimant, distantes l'une de l'autre de 10 millimetres. Une image de la flamme etait projetee sur la fente du spectroscope par un objectif double. La quantite d'oxygene introduite dans cette flamme permettait de regler la temperature de facon a donner aux raies spectrales D_1 et D_2 l'apparence voulue.

"Dans ces conditions, les raies sodiques D_1 et D_2 etant d'abord peu larges et non renversees avant le passage du courant d'aimantation, deviennent immediatement *plus brillantes, plus longues et plus larges* aussitot que l'electro-aimant est mis on activite.

"Si les raies brillantes D_1 et D_2 sont deja elargies, l'electro-aimant etant inactif, elles deviennent plus larges encore et *se renversent* (c'est-a-dire qu' une raie noire parait au milieu de la raie brillante elargie) pendant le passage du courant d'aimantation.

"Si les raies sont deja elargies et renversees, l'elargissement de la raie brillante et de la raie noire devient beaucoup plus considerable.

"Ces phenomenes, *qui disparaissent instantanement lors de l'interruption du courant,* peuvent etre observes, mais avec moins d'intensite, sur la raie rouge du potassium, du lithium, sur la raie verte du thallium, etc., lorsqu' une minime quantite de ces metaux ou d'un de leurs sels est placee sur le support de charbon.

"Enfin, les armatures coniques de l'electro-aimant etant remplacees par les armatures meplates, de maniere que toute la longueur de la flamme sodique seit comprise entre ces armatures, les raies D_1 et D_2, prealablement renversees et elargies, presentent un *double renversement* (c'est-a-dire l'apparition d'une raie brillante au milieu de la raie noire elargie), lorsque l'electro-aimant est en activite."

III.

Extract from article in Astro. Phys. Jr., February, 1899, by Perot and Fabry.

"* * * when the light is complex it is easy to obtain a precise measure of the ratio of the wave-length of the radiations which constitute it; let there be two radiations of nearly equal wave-length λ and $\lambda - \varepsilon$. The distances between the silvered surfaces is in-

creased until the discordance between the two systems of rings is complete. Then if e is the distance between the surfaces (which is given with sufficient accuracy by the micrometer) we have

$$\frac{\varepsilon}{\lambda} = \frac{\lambda}{4\varepsilon}$$

"* * * This method is also readily adapted to the study of the change of wave-length of a given line, on condition that the radiation be sufficiently monochromatic; in such a case a comparison can be made of two sources emitting, for instance, in the one case the altered radiation and in the other the normal radiation, attention being directed to the change in the appearance of the rings produced by the two sources successively."

* * * * * * * * * *

NOTE.—With the interferometer the ray travels the distance between the plates twice and hence $\Delta = 2e$. Therefore the equation for the interferometer becomes

$$\frac{\varepsilon}{\lambda} = \frac{\lambda}{2\Delta} \text{ or } \varepsilon = \frac{\lambda^2}{2\Delta}.$$

THE EFFECT OF MAGNETIZATION UPON THE ELASTICITY OF RODS.

BY J. S. STEVENS AND H. G. DORSEY.

IN the PHYSICAL REVIEW, Vol. II., No. 4 and Vol. III., No. 6, is described a series of important experiments which show the relation between temperature and elasticity in a wire. In one of the papers the statement was made that the results seem to indicate that the magnetizing effect of the current through the wire increases the modulus of elasticity. The increase in temperature in the wire was produced by sending a current directly through it, and also by sending a current through the helix which surrounded it. The author stated that "the magnetization produced by the first method had no appreciable effect on the result, and that if there is any difference in the effects produced upon the elasticity of a wire by magnetizing it, that difference is too small to be detected with any certainty by this experiment."

This paper contains the results of some experiments whose object was to test the effect of magnetization upon the modulus of elasticity by the application of interference methods of measurement.

The accompanying figure will make clear the method of operation. A series of carefully prepared rods[1] whose dimensions are given below, were in turn supported in the ordinary manner for determining the elastic modulus at points 3.2 cm. from their ends on adjustable knife-edges. In the center of the rod suspended from a hook was the load causing the deflection, and on the upper surface one of the mirrors of an interferometer. Surrounding the rod was first an air space, then a chamber for the passage of a stream of water, and on the outside two series of coils having a resistance of

[1] The same rods were used by Mr. C. P. Weston in his experiment described in the PHYSICAL REVIEW for May, 1899.

54.4 ohms each. When the rod was bent by the deflecting weight the interference fringes were found in the usual manner. A sodium lamp was used as the source of light radiations. It is obvious that any change in the modulus of elasticity due to magnetizing the bar would produce a corresponding motion in the fringes seen in the mirror.

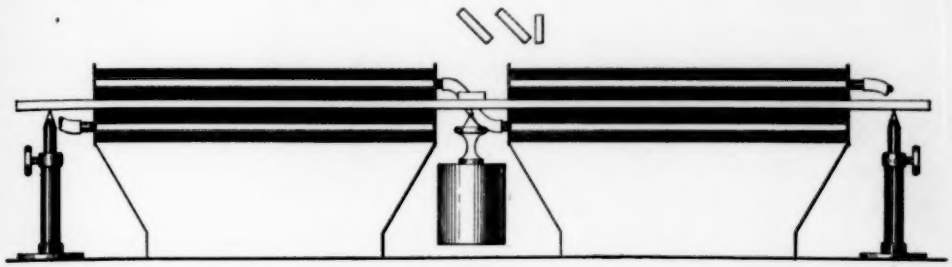

Fig. 1.

The great source of error to be guarded against in this work was the effect on the modulus due to heat. That this was eliminated will, we think, appear from the following considerations:

(*a*) A stream of water was caused to run through the chamber between the coils and the rod while the observations were made.

(*b*) The motion of the fringes appeared to be instantaneous when the current was turned on. When the circuit was kept closed for some time a creeping motion of the fringes (probably due to temperature changes) was observed.

(*c*) A copper bar of the same dimensions as those previously used was substituted, and no such instantaneous motion of the fringes was observed.

(*d*) The fringes came back to their initial position immediately when the current was turned off, when the steel rod was used.

(*e*) A thermometer reading by estimation to hundredths of a degree showed no appreciable change of temperature in the air surrounding the rod while the displacement of the fringes was being measured.

Among the difficulties encountered were:

(*a*) The arrangement of the mirrors so as to get good fringes. The conditions for producing interference were extremely unfavorable as the adjustment of the mirror on the bar had to be made en-

tirely by hand. It was supported on wax of such a consistency that it could be easily moved, but when once adjusted it kept its place. The difficulty here referred to, however, was one which needed only practice and patience to overcome, and whenever the observations were recorded the fringes were sufficiently distinct.

(*b*) Although the apparatus was mounted in a basement laboratory, on a stone slab supported by a brick foundation which did not come in contact with the floor or any other part of the building, a clock striking four stories above it caused a rhythmical motion of the fringes. It may be judged from this illustration that the work had to be done at such times as we could find the building free from ordinary disturbances.

(*c*) Another difficulty was encountered at first arising from the use of homogeneous light, and the consequent similarity of the fringes. With the mirror adjustments used here it would have been next to impossible to have obtained the colored fringes, which may readily be identified; but it was soon found that the displacements were never of an order of magnitude greater than one wave-length, and therefore the necessity of identification was avoided.

The following data were employed:

Length of rods,	66.3 cm.
Distance between knife-edges,	60.0 "
Breadth of rods,	1.0 "
Thickness of rods,	0.54 "
Length of magnetizing helix,	53.0 "
Number of layers of wire,	9.6
Number of turns of wire,	7026.
Minimum current used,	0.12 amp.
Maximum current used,	0.82 "
Number of turns per cm.,	132.

In the tables which follow are shown the current, the magnetizing force, the intensity of magnetization and the accompanying displacement of the fringes. In every case the direction of displacement indicated an *upward* movement of the mirror, and hence an *increase* in the modulus of electricity.

TABLE I.

STEEL BAR. LOAD 1K.

Current in amperes.	Magnetizing force.	Intensity.	Displacement in wave-lengths.
0.46	77.5	A nearly uniform	0.06
0.54	89.6	intensity	0.15
0.57	93.8	of about 700.	0.20
0.60	99.6		0.25
0.64	106.2		0.38
0.66	108.7		0.45
0.68	112.9		0.50
0.71	117.9		0.50
0.75	124.5		0.63

TABLE II.

STEEL BAR. LOAD ½ K.

Current in amperes.	Magnetizing force.	Intensity.	Displacement in wave-lengths.
0.44	73.0	A nearly uniform	0.06
0.45	74.6	intensity	0.06
0.46	77.5	of about 700.	0.06
0.62	102.9		0.13
0.64	106.2		0.19
0.65	107.9		0.25
0.66	109.6		0.25
0.68	112.9		0.31
0.71	117.9		0.50
0.75	124.5		0.50

TABLE III.

WROUGHT IRON BAR. LOAD 1 K.

Current in amperes.	Magnetizing force.	Intensity.	Displacement in wave-lengths.
0.12	19.9	389.7	0.08
0.15	24.9	516.5	0.22
0.27	44.9	735.2	0.28
0.33	54.1	838.2	0.35
0.38	61.3	.....	0.38
0.54	89.7	.....	0.48

TABLE IV.

WROUGHT IRON BAR. LOAD ½ K.

Current in amperes.	Magnetizing force.	Intensity.	Displacement in wave-lengths.
0.16	26.6	615.1	0.20
0.33	54.8	730.0	0.50
0.43	71.6	838.2	0.63
0.60	99.6	868.8	0.75
0.76	125.9	1075.0	0.88

DISCUSSION OF RESULTS.

The difficulties encountered in making these observations, and the fact that it was necessary to make them quite rapidly conspired to render the results recorded in the last columns of the tables rather unreliable as quantitative measurements. So far as practicable, however, they represent the mean of several observations taken by each of us. If they were plotted either with the magnetizing force or the intensity of magnetization they would not yield a straight line or any other regular curve. In every case, however, an increase of current was accompanied by an increased displacement. In the case of the steel bar it was necessary to keep the current within a limited range, and as shown in the tables the intensity remained nearly constant. With the wrought iron we were able to use a greater range of current and secured a greater deviation in the displacement column.

The following may be set down as the results of the experiment:

(*a*) The modulus of elasticity of wrought iron and steel increases with magnetization.

(*b*) In the case of steel little difference was observed for loads of 1 K and ½ K. In the case of wrought iron the smaller load gave the greater displacement when equal magnetizing forces were used.

PHYSICAL LABORATORY, UNIVERSITY OF MAINE.

ON FREEZING AND BOILING WATER SIMULTANEOUSLY.

By R. W. Quick.

MANY lecturers in physics perform annually the well-known experiment of placing a small quantity of water in a shallow dish under the receiver of an air pump and by exhaustion reduce the pressure below the vapor pressure of ice at 0°C. or 0.46 cm. when, if everything works properly, the water will be seen to boil and freeze at the same time, the lowering of the temperature being caused by rapid evaporation.

But this experiment requires a pump with automatic valves to attain sufficient exhaustion, the very best of thermal insulation from the bed-plate of pump, and some drying agent to absorb the vapor; and even under the best of conditions the quantity of liquid used must be so extremely small as to render the experiment not easily seen by a class.

In a recent lecture to a class in heat I accomplished the experiment in a manner which, I think, is novel and which is infinitely more satisfactory. The great advantage in this method is the large quantity of water which can be used, and the violence with which the ebullition occurs simultaneous with its freezing.

A flask made of good, strong, thin glass of about 500 c.c. or a liter capacity is nearly filled with water, and its contents boiled for at least an hour so as to insure the removal of all air from the flask. While still boiling violently the flask is quickly corked with a rubber stopper and the flame immediately removed. After inverting the flask cold water is poured on it, causing the water to boil. This will continue till the temperature of the water in the flask reaches a point nearly equal to that of the water applied. (This part of the experiment is a well-known one.) If ice water be applied to the flask the water in the flask will continue to boil till its temperature reaches about 3° C. Of course, there is no "boiling away," as the

vapor, after it is formed, is again condensed when it strikes the cold walls of the flask. In this experiment it is to be observed that the fall in temperature of the water in the flask is not due to evaporation, but is solely accomplished by the cold liquid applied to the outside of the flask.

The process is continued from this point by the application of a cold liquid. The liquid I used was ether in which was placed a large quantity of solid carbon dioxide which can easily be obtained from the commercial carbonic acid gas contained in cylinders under 55 atmospheres of pressure, and used for charging soda fountains. When a sufficient quantity of the solid is placed in the ether it assumes a constant temperature of $-75°$ C. It is necessary to use only about 100 c.c. of ether contained in a 150-c.c. glass beaker. Pouring this liquid upon the inverted flask, which must be supported in position by wood supports, and allowing the liquid to run down the neck of the flask, the water begins to boil immediately and continues to do so as the temperature of the water falls to the freezing point. This occurs in a few seconds after the cold liquid is applied. At this point steam will be seen to freeze on the walls of the flask, making it appear that the flask is cracking. Soon after bubbles of steam will be seen to have an envelope of ice formed about them just as they break through the surface of water and in a short time a layer of ice forms on the water through which bubbles of steam attempt to pass on rising to the surface. Ice also forms at the neck of the flask.

At this point I ceased pouring on the ether for fear the flask would burst due to the freezing of water in its neck.

Of course it is of the utmost importance to have all the air expelled from the flask before corking, else the pressure might be above 0.46 cm., in which event no amount of cooling would cause the water to boil and freeze simultaneously.

GEORGIA SCHOOL OF TECHNOLOGY, ATLANTA, GEORGIA.

NEW BOOKS.

Scientific Papers. By P. G. TAIT, Sec. R. S. E. Vol. I. Cambridge University Press. New York, The Macmillan Company.

The publication, under the auspices of a great university, of the collected works of a scientific man, is in itself a sufficient indication of the distinguished character of his investigations and of the high regard in which they are held by competent judges. The field that Tait has occupied is in one respect unique. His writings cover indeed, a wide range in mathematical and physical subjects, and his name will always be associated with those of the most notable workers in the modern development of physical science and physical ideas, but he also stands out prominently as the great successor to Hamilton in the development of quaternion analysis. A large portion of his investigations has been conducted by the aid of that analysis and have resulted not only to the advantage of the subject itself, but have also imparted to physical subjects new ideas and developments that are constantly employed even by those who have no knowledge of quaternions. It is hardly possible for the ordinary analyst to estimate the influence which the development of quaternions has had upon the mathematical and physical conceptions of the time. It has, indeed, given them an entirely new aspect and character, and has very greatly contributed by its natural methods of attacking problems, to the removal of the scientific disease of phasia or want of direct and visible apprehension. In all the developments of Tait, the physical and visual side remain predominant, and it is because of this natural desire to see things as they are, that the quaternion methods have appealed to him most strongly. Of the articles in this volume that are especially noteworthy as developments both of quaternion and physical truths, we may note those on Fresnel's wave-surface, on electrodynamics and magnetism, and the potential of a closed circuit, on small displacements of the particles of a medium, on the rotation of a rigid body about a fixed point, on Green's and other allied theorems, on linear differential equations in quaternions, on orthogonal isothermal surfaces, etc. The important results in all these papers are put in such shape as to be comprehensible to the ordinary analyst and physicist, for it is the peculiar property of quaternion forms that they are intelligible to all when stated in words, involving as they do, only direct processes of geometry and physics. There are also valuable papers on many mathematical and physical sub-

jects that employ the quaternion analysis very little or not at all, such as first approximation to a thermo-electric diagram, on electrolytic polarization, on the law of frequency of error, on thermal and electric conductivity, on mirage, the pressure errors of Challenger thermometers, etc. The volume also contains the complete series of papers on Knots. These constitute the most important work in this subject, first considered by Listing. In order to bring these papers together, the practice of publishing the different papers in the order of their presentation to the public, has not been followed, so that under the title of Knots we have several long papers, some of which would, in their order of time, appear in succeeding volumes. The volume is interspersed with valuable and brief notes, and also with lectures and addresses on various subjects, which are interesting and have often been epoch-making in respect to the ideas involved.

In editing his own writings at the request of the Syndics of the University Press, Tait has neglected to note those papers that received prizes for special merit at the time of their publication. For example, the Keith Prize for the best communication on a scientific subject, communicated in the first instance to the Royal Society of Edinburgh (preference given to a paper containing a discovery), was awarded for the period 1867–69 to the paper, "On the Rotation of a Rigid Body About a Fixed Point," and for the period 1871–73 to the paper, "First Approximation to a Thermo-electric Diagram." These two papers are typical illustrations of the two lines of work pursued by Tait, and a brief synopsis of them will show the general character and trend of his different investigations, which are always purely physical, whether in quaternion or analytical form.

The purpose of the first paper is best explained by a brief quotation from the author's introduction: "Although it is very improbable that there remains to be discovered any new, and at the same time simple, fact connected with a question which has been elaborately treated by many of the greatest mathematicians of this and the preceding century, the employment of a new mathematical method may enable us to present some of their results in a more intelligible form, and with far less expenditure of analytical power than has hitherto been deemed necessary; and it may give us such an insight into the question that we shall be able easily to discover the mutual relations among the various processes which have been employed; so far, at least, as these differ in principle, and not merely in the peculiar co-ordinates assumed for the purpose of simplifying the equations. Such a method is that of *Quaternions*, which seems to be expressly fitted for the symmetrical evolution of truths which are usually obtained by the ordinary Cartesian methods only after great labour of calculation, and by modes of attack so indirect, and at first sight so purposeless, as to bewilder all but a very small class of readers."

The fundamental basis of the investigation is the almost instantly demonstrated property that "*if q be any quaternion, the operator of q ( ) q^{-1} turns the vector, quaternion or system, to which it is applied, about the axis of q through double the angle of q.*"

If α be the vector number of a line drawn from the fixed point to any point of the body in its initial position, and ω be the vector number of the same line at time t, it follows at once that $\omega = q\alpha q^{-1}$, where q is some function of the time.

The differentiation of ω as to the time gives

$$\dot{\omega} = V.\, \varepsilon q\alpha q^{-1}, \text{ where } \varepsilon = 2V\dot{q}q^{-1}.$$

This shows that the line whose number is ε is the axis of instantaneous rotation and that $T\varepsilon.dt$ is the amount of instantaneous rotation. The expression of these results in terms of any coördinates of the line ω is now simply a matter of substitution of the resulting value of q, multiplying out, and equating corresponding coefficients of i, j, k. The formulas of Rodrigues and Cayley are thus found by simple multiplication, and similar forms in other coördinate systems, some of which are simpler than those of Cayley.

In considering the motion of the mass, Lagrange's general equations of motion take at once the form $\Sigma.mV\omega\ddot{\omega} = \psi$, where m is the element of mass to which ω refers, and ψ is the vector couple acting at time t. This gives the integral

$$\Sigma.mV\omega\dot{\omega} = \int\psi dt, \text{ or } \Sigma m\omega V\varepsilon\omega = \gamma.$$

When no forces act, γ is a constant vector, and from this fact follows at once Poinsot's beautiful construction of the motion by the rolling of a central ellipsoid fixed in the body on an invariable plane. Some very simple eliminations give the above equations in the form

$$2\dot{q} = q\varphi^{-1}(q^{-1}\gamma q)$$

which is a differential equation for the unknown quaternion q that fixes the position of the body at any time t. φ is a linear vector function depending only upon the initial position of the body and the distribution of mass in that position, and γ is the supposedly known couple acting at time t.

Tait says, "It is hardly conceivable that any simpler or more easily interpretable equation for q can be presented until symbols are devised far more comprehensive in their meaning than any we yet have."

The strain function φ is shown to pertain to the momental ellipsoid of the body, so that if i, j, k are units along the principal axes of the body in its initial position, and A, B, C, the movements of inertia about those axes, we have

$$\varphi\rho = -(AiSi\rho + BjSj\rho + CkSk\rho).$$

The article continues with the discussion of the integration of the above equation, the determination of the equations that have resulted from the labors of Euler and others, and various new equations, the solution for a homogeneous solid of revolution about a fixed point in its axis not the center of gravity, the equations of precession and nutation, etc.

"First approximation to a thermo-electric diagram" is the culumination of a series of theoretical and experimental papers whose results have a standard value in the subject. The principal results are given in Maxwell's Electricity and Magnetism, Vol I., Art. 254. In an early paper Tait had deduced from considerations regarding dissipation of energy that what Lord Kelvin calls the specific heat of electricity in a conducting substance should be, like thermal resistance, directly proportional to the absolute temperature, being for some substances negative. With a view of testing this theoretical result a number of experiments were conducted for the determination of the electro-motive force in various thermo-electric circuits through wide ranges of temperature. The resulting curves were found in all cases to be excellent parabolas. This accorded with the theoretical conclusion above, which makes the second temperature rate of change of electro-motive force a constant. The paper gives a synopsis of investigations and experiments that led up to this result, and devises a thermo-electric diagram, whose abscissas represent the absolute temperature of one junction of two metals, the other being maintained at constant temperature, and whose ordinates represent the temperature rate of change of the electro-motive force at the given temperature. The corresponding curves should therefore be straight lines, but in order to compare all substances with each other, they are taken with reference to a certain substance whose specific heat of electricity is zero, and which is therefore represented by the axis of abscissas. The experiments of Le Roux seem to show that lead is very approximately such a substance. The lines of the diagram then show the rate of charge of electro-motive force of the various substances in circuit with lead, and should be very approximately straight lines of positive or negative slope corresponding to their specific heat of electricity coefficient. The difference between two ordinates at any temperature is then the rate of change of electro-motive force in a circuit between them, at that temperature. The rectangle of this difference and the abscissa of absolute temperature is the Peltier effect at the junction. The intersection of the two lines is therefore at the temperature of the so-called neutral point. The electro-motive force between two metals when its junctions are at different temperatures is proportional to the difference of the areas of the triangles formed by the diagrammatic lines of the substances and the ordinates at the two temperatures.

One peculiarity of the diagram is that certain metals, for example

nickel, have a broken diagram, the separated portions being very approximately straight lines, which seems to show, as Tait remarks, that some bodies take successively different states at certain critical temperatures, retaining their thermo-electric properties nearly unchanged from one of those critical points to another. The experiments indicate such a critical temperature for iron at a low red heat, and Tait calls attention to the fact that other changes may be expected to take place in iron at this temperature besides the above thermo-electric one, and the sudden change of length of iron wire at this temperature observed by Gore and the sudden glow observed by Barrett that occurs simultaneously.

It would give me pleasure to outline many papers in this volume and to point out the gain in brevity, clearness, and simplicity of treatment that results from the use of the quaternion analysis, but I have already reproduced enough to indicate the distinctive features of the volume, and can only say in conclusion that I hope it may happen to others as it has often happened to myself, that the quaternion investigations of Professor Tait have been a revelation as to the true meaning of the physical part of the subject.

ARTHUR S. HATHAWAY.

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Physical Problems and their Solutions. By A. BOURGOUGNON. Pp. iv+224. New York, D. Van Nostrand Company, 1897.

This is a collection of 215 simple problems in physics, to each one of which the numerical solution is given in full The subjects of electricity and magnetism are excluded altogether, so far as problems are concerned; there being merely a brief statement of a few fundamental laws, such as Coulomb's law and Ohm's law at the end of the volume. British measures and the metric system are used indiscriminately throughout, a bad practice for which the author may, however, find his warrant in the example set by the Regents of the University of the State of New York. Some of the problems contained in this volume are indeed taken from their papers, and in the appendix a special list of "*Regents' questions*" is given.

E. L. N.

Ostwald's Klassiker der Exakten Wissenschaften. Nos. 61, 63, 72, 75, 76, 79, 80, 81, 82, 83. Leipzig, Wilhelm Engelmann, 1895 and 1896.

We have before us the above numbers of the series of Ostwald's reprints and translations of the classics of the exact sciences. In these days when every scientific man reads French, German and English with equal ease and is able in an emergency to translate for himself the substance of papers published in Dutch, Danish, Swedish and Italian, one cannot but

wonder that scientific men should find the time to translate into a single language the numerous monographs included in Ostwald's series. There is, however, no one of the treatises included in the list before us which is not well worth being reprinted and, for that matter, of being translated into German, and the thanks of the scientific world at large are certainly, due to any one who is willing to undertake the task of collecting and reissuing so large a number of valuable papers and thereby rendering them more accessible than they have been in the past.

E. L. N.